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Identifying the Potential Environmental Impacts of Engineered Nanomaterials

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Identifying the Potential Environmental Impacts of Engineered Nanomaterials

By

Therese Garvey

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy in Sustainability

Department of Sustainability
Golisano Institute of Sustainability
Rochester Institute of Technology

January 2016

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Identifying the Potential Environmental Impacts of Engineered Nanomaterials

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Therese Garvey

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SUSTAINABILITY PROGRAM
ROCHESTER INSTITUTE OF TECHNOLOGY
January 2016

ABSTRACT

Golisano Institute for Sustainability

Rochester Insititute of Technology

Degree Doctor of Philosophy

Program Sustainability

Name of Candidate Therese Garvey

Title Identifying the Potential Environmental Risks of Engineered Nanomaterials

Engineered Nanomaterials (ENMs) are increasingly manufactured and incorporated into a diverse array of consumer products and industrial uses. While ENMs are touted for their technological and efficiency benefits, the potential impacts of increasing emissions and exposures to ENMs are poorly understood. This dissertation takes a critical look at the current knowledge in impact assessment of nanomaterials. First, the current metrics for impact assessment of traditional methods are compared with the proposed set of metrics necessary for nanomaterial impact assessment. Next, in order to understand the potential environmental impacts in context, characterization factors for four case study nanomaterials are modeled using physicochemical data from literature sources and adjusting the USEtox method as necessary. Then cradle-to-gate life cycle assessments are performed for the production of case study nanomaterials to understand the primary drivers of environmental impact. Last, the larger context of nanomaterial production is considered by forecasting a potential use of CNTs in lithium ion batteries over the next 25 years. Current policy issues are discussed within a life cycle context for the nano-enabled lithium ion battery.

The results demonstrate that in most cases nanomaterials do not contribute a significant impact to the total in LCA. In contrast, energy production for these materials is found to be the primary driver of impact in cases where inherent nanomaterial toxicity is low. Electric vehicles and energy storage were found to be the primary drivers of CNT production for lithium ion batteries in both forecasted scenarios, indicating that despite the current debate over how to use toxic chemical regulations to best control risk, regulations over electricity and energy production could better target the overall environmental impact in most cases. Furthermore, there is potential for future regulations to incorporate novel metrics so that life cycle impact assessment can inform environmental policy.

ACKNOWLEDGEMENTS

I would like to express my very great thanks to my academic adviser, Dr. Gabrielle Gaustad, for allowing me this opportunity, helping me find a meaningful field of research and pushing me forward throughout the past years. I absolutely could not have achieved this without your guidance.

Thanks also to Dr. Callie Babbitt for your always valuable and insightful feedback. Advice given by Dr. Eric Hittinger and our external examiner Dr. Christy Tyler was also instrumental to the contributions to the final product.

Next, thank you to the Office of Pollution Prevention and Toxics at the US EPA for giving me the incredible experience of putting into practice the sustainability coursework and research during my internship. Thanks especially to my mentor, Phil Sayre, for exposing me to many more valuable resources in my field and for his continued support and guidance.

Last, thank you to my friends in GIS, especially Xue Wang and Lourdes Gutierrez, for being my allies in the office and out, my friends outside of GIS for helping me decompress. Last, thank you is due *especially* to my family for their constant love and support.

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CHAPTER 1. Introduction

1.1 Introduction to Nanomaterials

Nanomaterials hold much promise for technological innovation and the global market for nanomaterials has already reached the multibillion dollar level[1] . While varying in shape and elemental compositions, the common feature of all nanomaterials are that they have at least one dimension in the nanoscale (1-100 nm). Nanomaterials are credited for improvements in medicine including imaging and drug delivery[2] [3] [4], enabling clean transportation and renewable energy storage, vital for intermittent sources such as wind and solar[5], environmental pollution remediation[6], and for improvements to the functional and structural quality of a wide array of consumer products. The Woodrow Wilson Institute for Scholars maintains a database of products in commerce, the Project on Emerging Nanomaterials (PEN) Consumer Products Inventory (CPI) [7]. The number of nanomaterial-containing products in the CPI increased 520% from 2005 to 2010 and included products including children's toys, house and garden, appliances, electronics and personal care. Each of these categories has seen significant growth in the years since the CPI's introduction in 2005. Furthermore, many applications of nanomaterials are still at the laboratory or research and development stages, indicating that the number of applications and sheer volume of nanomaterials themselves will continue to grow as these applications become commercially available.

As the number of applications increases so too will occupational, consumer and environmental exposure to these materials. Because the types of products and applications are varied and increasing in diversity, exposure to engineered nanomaterials

will occur through all pathways (oral, inhalation, dermal, ambient, and environmental) and at all life cycle stages of the material or product (manufacture, use, and end of life). While nanomaterials may advance technology, medicine, and remediation, there are unintended consequences with the introduction of these emerging materials into human and environmental systems if proper risk-reducing strategies are not employed. Considering environmental, health and safety issues and policies that can reduce these issues early in the technology's development will help integrate the new technology into society and prevent backlash or reactionary regulation. As much environmental policy in the United States historically has been reactionary, an analysis of similar past problems with an informed understanding of the potential hazards presented by nanomaterials may help to reduce EHS issues before they become an environmental disaster and require these reactionary regulations.

1.2 Risk Assessment

Enacting and enforcing risk management policies requires a quantifiable risk. Common paradigms characterize the steps of risk assessment as hazard identification, dose-response assessment¹, and exposure modeling. Hazard identification is the observation of adverse effects given some exposure to a stressor, in this case nanomaterial or nanoparticle. Effect assessment requires measuring and modeling a quantitative relationship between exposure to the stressor and the effect. Quantitative risk is the product of exposure probability and the probability of an adverse effect at that

¹ NB: In risk assessment, the second facet of risk assessment is usually referred to as impact but herein the term "effect" is used to avoid confusion with other uses of the term "impact."

exposure level. In order to explore the challenges in risk assessment for nanomaterials as they stand, the methods in each of the risk assessment steps are outlined.

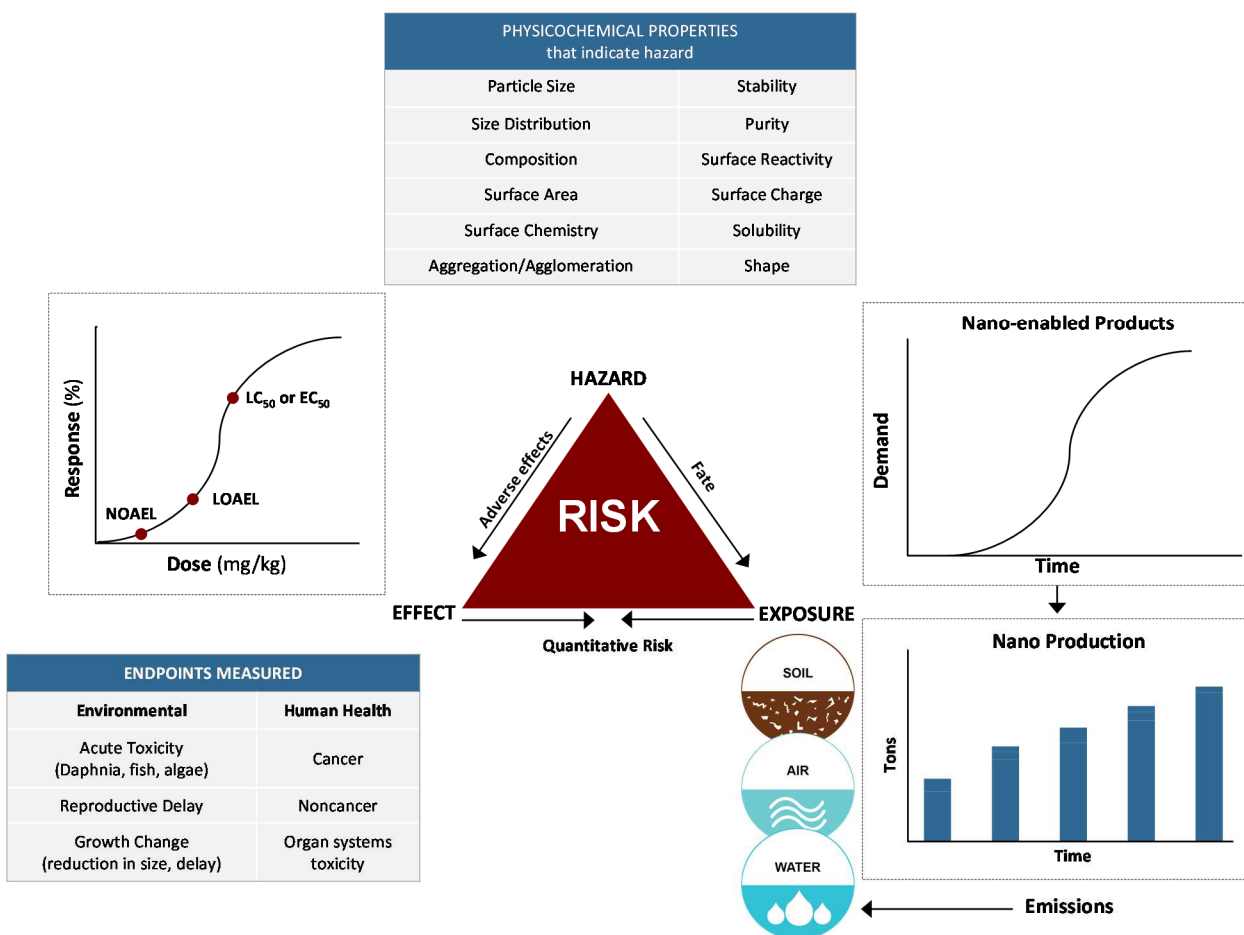


Figure 1.1 Risk Management Paradigm which outlines how the three facets of risk interconnect and a depiction of the steps involved in each.

Hazard Identification involves drawing correlations between the presence of a chemical and an adverse outcome. Those physicochemical properties that have been identified as relevant to nanomaterial hazard identification are included in the uppermost table. The relationships between the chemical dose and the adverse effect experienced are quantitatively measured and extrapolated in Effect Assessment. Exposure Assessment involves modeling and measuring the fate and transport of the chemical

hazard throughout its life cycle to predict where exposures to humans and the environment will occur.

1.2.1 Risk Assessment Steps

The preliminary step of risk assessment is hazard identification, the observation of an adverse effect caused by exposure to a chemical stressor. Effect assessment then consists of testing and quantifying the relationship between exposure and the adverse effect, characterized by a dose-response relationship. The overarching findings from human health and environmental effect assessment literature are found in Section 1.3. Exposure assessment consists of determining how and in what life cycle stage a given nanomaterial will likely be released and characterizing dispersion into the environment by identifying relevant pathways, residence time, and degradation whether by modeling or empirical studies.

1.2.2 Methodological Challenges to Risk Assessment

Exposure potentials for nanomaterials are significantly influenced by aggregation and agglomeration, transformations in the environment [8], and nanomaterial physicochemical properties. A reformulation of existing exposure models to incorporate these considerations is difficult without a good understanding of interactions at the nanoscale. Traditional exposure models use a mass metric, while the influence of physicochemical properties in the fate and transport of nanomaterials indicates a need to incorporate these properties into the models [9]. The US EPA has proposed the development of physicochemical metrics in quantifying toxicological dose, as opposed to

the traditional mass metric[10], and the European Union has adopted a "number of particles" metric for future regulation[11].

Life cycle thinking is also vital in exposure assessment, as exposure probability depends on the integration of the nanomaterial into the product as demonstrated by the findings of a model developed by [12] and further study by [13]. These models show that nanomaterials used as coatings, in textiles, and in cosmetics have a high probability of exposure to humans or the environment during consumer use[12], while nanomaterials that are contained *within* a product have exposure pathways that occur mainly during production or end-of-life (EoL) management. Clearly, CNTs used in batteries and “smart textiles”[14] will disperse into the environment through different mechanisms, i.e. through disposal or use, respectively. It is vital to consider the whole product and life cycle as opposed to focusing only very narrowly on properties of a reference nanomaterial used in a product.

Despite the great interest and amount of work being done, challenges in nanotoxicology remain. In many cases nanomaterial effects differ substantially from the effects of the respective bulk material, and so predictive patterns of impact still elude researchers[15] [16]. The practice of testing a single type of nanoparticle in a medium and measuring a single impact can be expensive and slow [17] [18] and will not keep apace with the rapid development and deployment of nanomaterials and the resulting increase in exposure possibilities. In response, predictive toxicological paradigms and high throughput screening have been proposed [19] [20] [21] to accelerate the process by predicting toxicity and then performing strategic toxicity tests.

The second major challenge in nano-risk assessment is the importance of using more sophisticated metrics [22]. Traditional toxicology uses mass or concentration (mass/volume) to quantify dose, however for nanomaterials the response may be better characterized by particle size, surface area [16] or particle number [23]. Because of results like these, researchers now recognize the need for extensive physicochemical property characterization before beginning and *throughout* testing. One study [24] found by looking at over 400 toxicity studies, a set of 28 physicochemical properties that has the greatest influence the result; these are depicted in Table 2.1. Researchers, governmental and standards organizations have begun to coalesce around minimal information characteristics, such as those used by the Nanomaterial Registry, a project funded by the National Cancer Institute (NCI): particle size, size distribution, aggregation/agglomeration state, shape, purity, surface chemistry, solubility, surface reactivity, stability, surface charge, surface area, and composition [25] , [26], [27], [28]. These properties at a minimum must be characterized before and during study in order to understand the changes undergone and the comparability between studies.

A third challenge is a lack of standardization in nanotoxicology studies and the inadequacy of current toxicology tests for nanomaterials. Though the use of rodents as proxy for human effect has always been an issue in toxicology, the validity of extrapolating rodent results to humans for nanomaterials is particularly troubling [29] [30] given the number of other factors that create uncertainty. The high cost of sophisticated detection methods plays a role in the quality of toxicology studies. In aquatic studies, dispersion is achieved through the use of surfactants or sonication, which

has been questioned. Further recommendations for adjusting traditional aquatic toxicity methods have been recommended [31].

1.3 Impacts of Nanomaterials

Besides the challenges in risk assessment of nanomaterials, there are potential impacts from direct exposure to nanomaterials. While environmental impact is a subcategory of sustainability, it is itself quite broad. It is desirable to be able to state categorically an overall positive and negative impact on the environment of nanomaterials, it is difficult to do so because of the various endpoints that can measure an impact to the environment. The following diagram shows which types of endpoints can be considered part of the overall “environmental impact” landscape, and how aquatic freshwater ecotoxicity fits into the overall paradigm. In short, while complex in itself, aquatic freshwater ecotoxicity is a first step in modeling and describing ecotoxicity, which in itself is a subcategory of environmental impact, but it is not nearly comprehensive in describing ecotoxicity. It is, however, often used as a proxy for ecotoxicity.

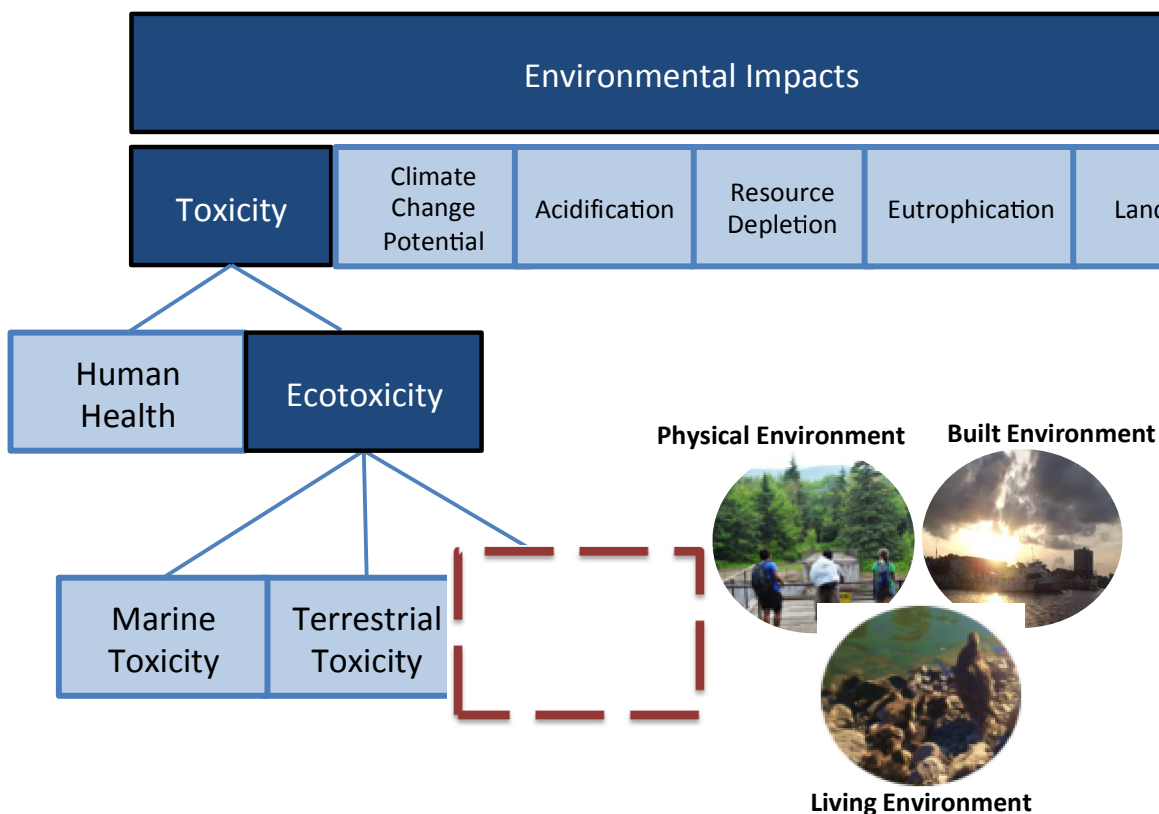


Figure 1.2 Environmental Impact: Categories and Subcategories. *Environmental Impact is a broad category of impacts to the environment, one of which is toxicity. Ecotoxicity and aquatic freshwater toxicity are subcategories of toxicity. Risk assessment can focus on environmental impacts, measured by changes in the physical, built and living environments.*

To begin identifying the potential toxicity impacts of nanomaterials, the following sections summarize the human health and the environmental toxicity of nanomaterials found in the effect assessment literature.

Human Health Effects

Extensive research has been done to quantify the effects of inhalation of ENM. Inhalation of various nanoparticles results in their deposition onto parts of the tracheobronchial regions and lungs [15],[32]. Nanoparticle size has been shown to be related to the location of deposition [33], [34], [35], and translocation from the first

deposition to other organs has been observed. Concerns are still raised about the ability of nanomaterials to cross the blood brain barrier. Observed affected organs are the lungs, blood, brain, kidneys, liver or spleen [36], [37] [38], [22]. Among the observed effects of nanoparticle inhalation are increased respiratory and cardiovascular morbidity and mortality, fibrosis, chronic inflammatory lung disease, and cancer, which are influenced by nanoparticle characteristics including particle size distribution, aggregation, solubility, and surface characteristics [39].

Ingestion could occur after hand-to-mouth contact [40] though nanoparticle deposition would likely differ from inhalation. Once inside the stomach, nanoparticle chemical properties may change because of the change in pH [41]. From the stomach, nanoparticles can be taken up by the blood and translocated to the liver and the spleen [22]; given deposition, nanoparticles can disrupt cellular functions.

Dermal nanotoxicology assessments have shown oxidative stress, cellular and antioxidant depletion, loss of cell viability, and other cellular dysfunctions[42], [43]. While nanoparticles have been shown capable of penetrating the epidermis and the dermis [44], this is largely size dependent [41] in that smaller particles are more likely to penetrate further than large ones. Despite this evidence, the effects of dermal exposure to and ingestion of engineered nano- and ultrafine particles are generally believed to be less significant than that caused by inhalation [42], [43], [45]

Environmental Effects

Effects to wildlife and changes in environmental media such as soil, air and water are also possible. Nanoparticles have been shown to produce adverse health effects in

wildlife such as fish, daphnids, algae and other animals[46] [47]. Aquatic toxicity, often approximated by the effects to vertebrates (fish), invertebrates (daphnia), or plants (algae), has been given considerable attention. In fish, demonstrated effects include damage to surface tissues, gill injury, respiratory problems, and oxidative stress for carbon-based nanoparticles [48], [49]; metallic particles in fish may target gills, liver, and brain, with the associated toxic effects including oxidative stress and cellular dysfunctions [46, 47]. In daphnids, the demonstrated effects have been acute toxicity [50], [51], immobilization, reproduction and growth [52].

Other important environmental effects are changes in the biological and chemical properties of living and nonliving things such as bacterial growth in soil [53], and plant growth [54]; however, the mechanisms and broader impacts of environmental changes are still poorly understood. Changes to abiotic environmental media may in turn affect living things; for instance, a change in plant growth or toxicity may affect those populations reliant upon that plant for food. Because toxicological studies focus primarily on environmental organisms and animals, the implications on ecosystem health and dysfunction have not been explored in depth.

1.3.1 Key Parameters for Nanomaterial Impact Assessment

Researchers in the field of nanotoxicology understand that studies have suffered from a lack of characterization of relevant nanomaterial properties, as these properties often influence the behavior of NPs. In this way, seemingly identical studies can find different results if the materials used have different characteristics[26], of which researchers are unaware. Additionally, the dose metric has been identified as a

methodological challenge for nanotoxicology. Traditional dose metrics, such as mass, may not be the best metric to determine fate or toxicity of some nanoparticles; rather, surface area and number density have been identified as better predictors of probability of an adverse impact in some situations [55]. Therefore, knowing particle characteristics is essential to developing new metrics for dose-response relationships. Determining appropriate metrics by study type could be a key step in developing the field of nanotoxicology, impact assessment for nanomaterials, and subsequent RAs and LCAs.

To identify the best physicochemical properties for use with human health nanotoxicology studies, Oberdorster et al. [56] recommended that the following as general guidelines for consideration: the context of the study, the importance of a parameter within that context, and the feasibility of measuring the parameter. Standards making organizations [57], experts and other literature [58, 59] and the MINChar Initiative[60] have called for different sets of physicochemical properties, listed in Table 1.3, to be taken into account when performing nanotoxicology tests. Characterizing these properties is vital because multiple references have shown that one or more of these can be a better toxicological predictor than the traditional mass metric such as using surface area in rats [56]and for E. Coli and Daphnia Magna using a combination of particle concentration and surface charge [61].

Primary Properties	Additional Influential Characteristics
Particle Size*†	Bioavailable surface area
Size Distribution*†	Redox potential and properties †
Aggregation/Agglomeration State*†	Identity of contaminants
Surface Area (specific) *†	Conductivity
Shape (Morphology/Form)*†	Defect Density
Surface Reactivity*	Hardness
Solubility (water and biological)* †	Magnetic properties
Stability*	Optical properties
Purity* †	Major commercial uses †
Surface Charge* †	Method of production †
Elemental/molecular composition* †	Representative TEM picture†
Dispersability (dry/wet) †	Photocatalytic activity
Crystal structure/ crystalline phase†	Pour density†
Crystallite size†	Octanol-water partition coefficient†
Particle Concentration	Other relevant information
Density	
Porosity (specific) †	
Surface morphology/structure†	

* indicates those properties on the Nanomaterial Registry list

† are those properties required by the OECD guidance document

Others come from surveys of literature and expert meetings

Table 1.1 Physicochemical Properties Called for in Nanotoxicology [57],[58, 59] [60]

The difficulty in performing thoroughly characterized nanotoxicology tests continues after agreeing upon the relevant set of parameters. Besides handling the physicochemical parameters themselves, traditional toxicology testing methods require alteration. Handy recommends some best practices in testing ecotoxicology of nanomaterials. Notable recommendations are accounting for the differences in static vs. renewed test solutions, starvation vs. fed tests, the use of surfactants, which play a role in uptake by the organism and dispersion in the medium, and the use of sonication, which may change the properties of the nanomaterials themselves [62]. Furthermore, these organizations call for testing throughout the life cycle of the nanomaterial in order to understand the transformations undergone.

1.4 Policy Implications

Developing anticipatory policy for nanomaterials before the major uses of nanotechnology mature and reach peak deployment will aid the safe and sustainable implementation of these materials into the social, economic and environmental realms. Environmental policies are implemented to reduce the harmful impacts of a technology, but policies with teeth are often reactionary rather than anticipating impacts before they become problems. Policymakers must be careful to understand the specific interactions and transformations of nanomaterials with the environment since these will often differ substantially from larger sized materials. Anticipating these impacts will require a critical look at the current policy environment as it is or will be applied to nanomaterials and nanomaterial-containing products and the development of tools for risk and life cycle assessments for nanomaterials.

The current regulatory framework faces many challenges. Because there is no single “nano industry,” there are multiple agencies at the US federal level that will have to control nano-risk within their respective regulations. These issues exist at the state, federal (US EPA, FDA, CPSC, etc.), and multi-national (EU and OECD) regulations that have already begun to grapple with nanomaterials. Just as there are a number of types of products and applications for nanomaterials, they are regulated as different kinds of hazards. The US Environmental Protection Agency regulates nanomaterials by categorizing them as toxic chemicals, water and air pollution, and waste. The US Food and Drug Administration regulates their use as food additives or in cosmetics. The Consumer Products Safety Commission (CPSC) is concerned about user exposure to nanomaterials from products; the CPSC is working with the EPA to determine whether the amount of nanomaterials in commercially available products presents a hazard, particularly nanosilver in children’s products[63].

These policies either have already or will in the future face problems when agencies are asked to administer them for nanomaterials because they rely on models and metrics developed for larger (bulk) materials. For instance, chemical analogs and Quantitative Structural-Activity Relationships (QSAR) or ECOSAR relationships are often used to predict toxicity for risk assessment under TSCA. Toxicity for nanomaterials cannot be predicted using these models or existing exposure models since it has been demonstrated that the properties of nanomaterial toxicity differ from their bulk materials[15]. Predictive toxicology methods could be useful for use under similar regulations[20, 21], but it has yet to be seen if predictive models are sufficiently valid for administering and enforcing regulation.

1.5 Motivation

In order to help regulators understand the impacts of nanomaterials better and advance these methods the following research questions are addressed. First, current impact assessment models do not capture the important physicochemical properties of nanomaterials that drive toxicity. In the field of Life Cycle Assessment, past studies [64], [65] that involve a nano-enabled product do not quantify the impacts of nanomaterials themselves and have therefore *underestimate* the total impact. This is due to the complexity with modeling nanomaterial impact and exposure. Chapter 2 uses scenario analysis to define ranges for nanomaterial impact, and exposure. Then using these ranges, the analysis compares the possible magnitude of toxicity as a result of direct nanomaterial emissions with those impacts from embedded electricity and materials. This comparison helps contextualize the nanomaterial ranges in order to understand whether they are significant in the total production system. The results can also identify when nanomaterial emissions directly drive the impact of the production system and when nanomaterial emissions can be considered relatively insignificant.

While life cycle assessment gives interesting results, data limitations and the assumptions necessary generally force the practitioner to focus on a single nanomaterial or nanoproduct, whereas in reality production of nanomaterials is increasing dramatically and these impacts may become significant. Given the dramatic increase in demand for nano-enabled products and the significant amount of funding for developing these products, production of nanomaterials is already increasing dramatically. As with any developing market, there are often unforeseen changes in the system in which the market

operates and interacts. In the case of nanomaterials, and as will be demonstrated in Chapter 2, the primary drivers of environmental toxicity associated with nanomaterial production are generally not direct toxicity. Rather, the embodied energy and production electricity requirements will contribute the most significant part of ecotoxicity associated with many nanomaterial production systems. Chapter 3 looks at the unintended consequences of nanomaterial production at forecasted demand for a case study product. Chapter 3 additionally calculates the environmental impact from embodied energy and materials of increased volumes of CNTs. The analysis uses a life cycle framework for understanding existing regulations and their adequacy for controlling nanomaterial related risks now and at projected future scales.

CHAPTER 2. Categorizing the Primary Factors of Ecotoxicity in Nanomaterial Production

2.1 Introduction

Nanomaterials are materials characterized by their size, where at least one dimension lays in the nanometer range, 10^{-9} m. Their size confers many unique properties not found in bulk materials that provide unique optical and chemical performance. For this reason, nanomaterials are increasingly engineered and used in diverse applications across many product sectors including commercial products, energy products, medicine and environmental remediation. Despite the potential benefits of nanomaterials, some questions remain regarding the tradeoff between the production and environmental impact of these materials and their potential technological gains. Quantifying this tradeoff requires an understanding of the life cycle environmental impacts of these materials and the relative contribution of the upstream and direct nanomaterial emissions to their overall environmental impact.

As a decision-directed tool, life cycle assessment (LCA) is a natural choice for assessing the potential risks of nanomaterial use and emissions into the environment. Because their physical and chemical properties differ dramatically from their larger counterparts, fundamental characterization and analyses of nanomaterials, which would normally underpin predictive risk models, cannot keep pace with the rapidly increasing rate at which these materials are being developed and produced. Thus, life cycle impact assessment methods have not yet been developed for all nanomaterials, preventing the possibility of quantifying life cycle tradeoffs of nanomaterial-containing products. Many past LCAs performed for nanomaterial-containing products have omitted the impacts

caused directly by nanomaterials themselves[64] [65] thereby ignoring a potentially significant source of impact, and instead focusing primarily on the energy of production. In one case where nanomaterial ecotoxicity was modeled, findings showed that, at least for the case of carbon nanotubes, direct emissions contribute a negligible portion of the total toxicity[66]. The question remains: under what conditions do nanomaterials contribute a significant amount of ecotoxicity, necessitating that detailed impact assessment modeling be conducted in LCA of nano-enabled products, and in which cases can nanomaterial emissions be estimated or omitted from an LCA.

The lack of impact assessment models for nanomaterials is due primarily to variability and uncertainty in environmental fate and toxicity[64] and the role of physicochemical parameters in these factors. Nanomaterial toxicity varies with physicochemical properties and both toxicologists and LCA practitioners often do not possess the necessary chemical-specific data. The current study aims to identify ranges for nanomaterial emissions and impact based on current knowledge. Identifying and quantifying these ranges will allow the LCA practitioner to understand the implications of omitting direct nanomaterial emissions from impact assessment and enable a quantification of the extent to which nanomaterial impact contributes to the total environmental impact of the product into which they are incorporated. Therefore, this chapter will perform an impact assessments of four case study products outlined in Section 2.2 in order to understand which upstream and direct processes are associated with the greatest environmental impact, e.g., production of electricity, extraction of materials, or release of direct emissions.

2.2 Methods

2.2.1 Life Cycle Assessment Modeling

Nanomaterial impacts are characterized within two categories: 1) upstream or “embodied” impacts due to nanomaterial production and 2) direct impacts due to nanomaterial release. The upstream impacts are modeled with existing life cycle inventory (LCI) data. Next, existing life cycle impact assessment (LCIA) models are adapted to calculate the necessary characterization factors for assessing the direct impacts. These characterization factors are determined on the basis of a comprehensive literature review.

2.2.2 Case Study Selection

Future analysis in this chapter focuses on the following selected case study materials: silver nanoparticles (n-Ag), nano-titanium dioxide (nano-TiO₂), single wall carbon nanotubes (SWNT), and 60-carbon spherical fullerenes (C₆₀). The case studies were selected based on their prevalence in risk assessment literature and significance in terms of consumer products, policy and important material characteristics. The most common nanomaterials in consumer products are nanosilver, carbon-based nanomaterials and titanium-based nanomaterials [67]. In terms of policy, many policy decisions have been made about carbon-based materials under TSCA [57] and nanosilver under FIFRA [68]. Furthermore, the nanomaterials chosen cover a potentially important cross-section of categories (metals, metal oxides, and carbon-based) so that the analysis can determine if these characteristics indicate ecotoxicity. Furthermore, their life cycle inventories are available in the open literature, making consistency and transparency possible. While C₆₀

fullerenes do not necessarily meet these criteria, they are included due to the similarities between these and SWNTs for comparison between carbon-based materials.

Carbonaceous Nanomaterials Single Wall Carbon Nanotubes (SWNT) are tubes comprised of graphene one wall thick. Specific advantages of SWNT are their tensile strength and young's modulus[69]. Potential uses are in semiconductors, batteries, hydrogen energy storage and others. Another carbonaceous nanomaterial of interest are C₆₀ fullerenes. Spherical fullerenes are molecules in the shape of hollow spheres commonly made of 60, 70 or more carbon atoms. They are currently used in cosmetics, skin creams, polymers, fuel cells, in lubricants, and organic photovoltaics [70].

SWNT and fullerenes can be produced using HiPco (High Pressure Carbon Monoxide), CVD (Chemical Vapor Deposition), Arc (arc ablation (carbon arc discharge)), Laser ablation and other methods. Fullerenes can also be produced using pyrolysis of naphthalene, and the arc vaporization of graphite [70]. Here the methods of production analyzed are carbon vapor deposition and arc ablation for SWNT production, and pyrolysis using toluene and arc ablation for fullerenes.

Nano-TiO₂ The second most common type of nanomaterial listed in the Project on Emerging Nanotechnologies' Consumer Product Inventory (PEN CPI) is titanium dioxide. Nanoscale titanium dioxide can be found in sunscreens, self-cleaning devices, UV-resistant materials, cosmetics, printing ink, chemicals, plastics, rubbers, wastewater treatment, for the degradation of pesticides, production of hydrogen fuel, as a photocatalyst, dye sensitized solar cells [71], [72]. The ratio of anatase to rutile compositions can vary in nano-TiO₂ samples. All available data, irrespective of differences in the anatase/rutile composition, for nano-TiO₂ was used in modeling.

Nanosilver Listed most commonly in the Consumer Products Inventory, silver nanoparticles have antibacterial properties that make them useful in textiles, consumer products, hand sanitizers and skin products, optical applications and conductive inks [73], [74]. They can be produced using grinding, a pulsed plasma process, reduction of silver ions, laser ablation or vapor deposition [75].

Appendix A contains the data from nanotoxicology studies used here. Each table contains information on the environmental medium (i.e. the plant or animal exposed), the most important physicochemical characteristic for each nanomaterial tested, the endpoint measured in the study, and the resulting data point (i.e. LC₅₀, EC₅₀ or other).

To align with these existing data, the system investigated in the LCA was limited to the upstream production phase (“cradle-to-gate”). Previous LCAs often do not contain information on nanomaterial emissions during the production processes, therefore emissions estimates in the present study are based upon synthesis yields, losses during production, and waste water treatment removal rates. In each case study, impacts are related to the functional unit of one kilogram of pristine nanomaterial (not modified or functionalized). In LCA, the functional unit provides the basis on which flows, emissions, and impacts can be compared. In the present case, a traditional “function” is not chosen, because these nanomaterials can be used in a wide array of final applications and because the ultimate goal is not comparison among materials, but rather investigation of trends and drivers within each case study material.

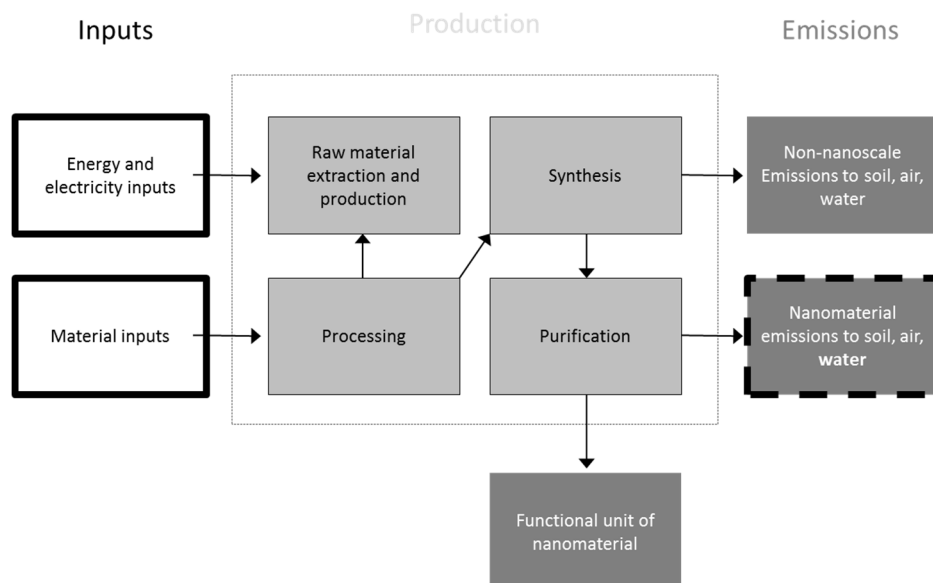


Figure 2.1: General Scope for LCA Modeling of the Four Case Study Nanomaterials. *All boxes are generally those that have been included in the LCI and LCIA of previous studies, excluding that with the dotted border. The specific contribution of this study is to incorporate nanomaterial emissions and their impact into LCA. More detailed scopes can be found in the supplemental information.*

2.2.3 Life Cycle Inventory Development

LCI data are taken from previous LCAs of the case study materials, specifically single wall carbon nanotubes [69], nanosilver [76], C₆₀ fullerenes [77] and nano-TiO₂ [78]. The additional information needed is the mass of nanomaterials emitted during the production process. In the absence of robust data about where and to what extent emissions occur, the realistic and worst case scenario approach are used. For this study, the “realistic” emissions are on the order of 0-5% of the total nanomaterials produced and are based upon the production method efficiencies. The worst case scenario assumes 100% of nanomaterials are emitted to freshwater. While an unrealistic assumption in typical applications, it may be relevant given the lack of specific policies ensuring environmentally sound disposal. Furthermore, some portion of these nanomaterials will

enter the aquatic environment at end of life, though this is not specifically modeled here. In this way, the worst case scenario acts to model the total life cycle emissions.

To understand the drivers behind each process block in the LCI, process level data are categorized according to the flowchart in Figure 2.2 B. The impact allocated to each material and energy input in the LCI are parsed by the emissions associated with the given material or energy block. These emissions are then sorted to categorize it as electricity, mining, waste treatment or other. Impacts arising from transportation are also isolated and categorized as transport. The electricity used during nanomaterial production is considered “direct electricity” or “production electricity. The data can then be categorized as embedded energy and electricity, production electricity, nanomaterial release, or other.

Table A.

Lifecycle Inventory

	Material Input A	Material Input B	Energy Input C	Energy Input D
	Total Impact of Material A = $\sum (E_{A,n})$ over x's	Total = $\sum (E_{B,x})$	Total = $\sum (E_{C,x})$	Total = $\sum (E_{D,x})$
Emission x1	$E_{A,x1}$	$E_{B,x1}$	$E_{C,x1}$	$E_{D,x1}$
x2	$E_{A,x2}$	$E_{B,x2}$	$E_{C,x2}$	$E_{D,x2}$
x3	$E_{A,x3}$	$E_{B,x3}$	$E_{C,x3}$	$E_{D,x3}$
x4	$E_{A,x4}$	$E_{B,x4}$	$E_{C,x4}$	$E_{D,x4}$

Table B.

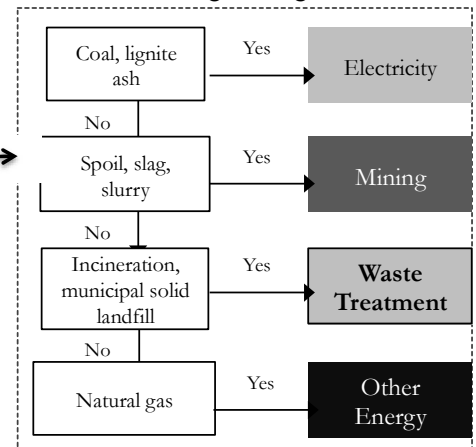
Flowchart Categorizing Emissions

Figure C.

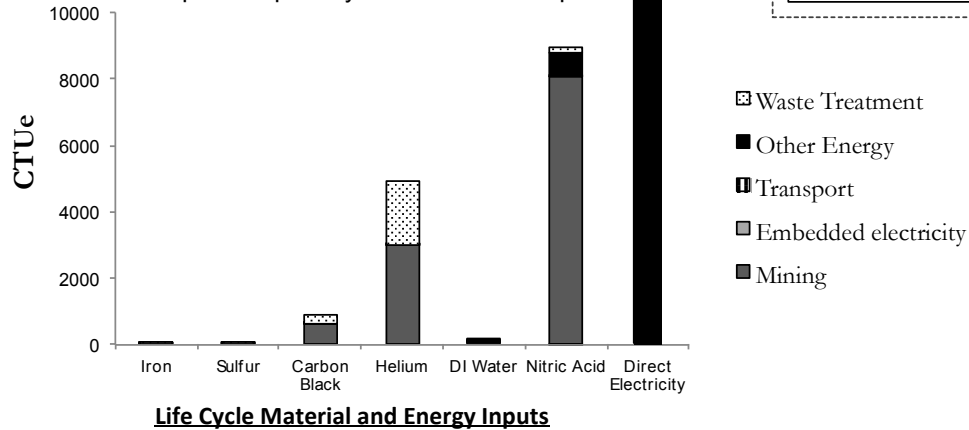
Graph of Impact by Emissions and Inputs

Figure 2.2 Categorization Flowchart Translating LCI into Drivers of Impact. The figure shows the relationship between LCI inputs (i.e. material and energy inputs) and the embedded emissions and activities that cause the impact allocated to each respective input. These embedded emissions are categorized according to the flowchart (Table B). The final result in the figure C displays the relationship between inputs, emissions, and ecotoxicity impact.

2.2.3 Impact Assessment Methods

A critical decision for the LCA practitioner is the choice of the impact category, since there are many different metrics, which represent environmental impact. LCA practitioners often rely primarily on Cumulative Energy Demand or Greenhouse Gas potential as impact categories, since ecotoxicity often correlates with these metrics[79]

The question unfolds in the present study as to whether this holds true for nanomaterial production and use given their unique properties. For this reason and for simplicity, freshwater aquatic ecotoxicity is the primary impact category used here. There is a considerable amount of uncertainty with toxicity impact categories whereas categories like CED and GHG potential are more consistent. The previous nano-LCAs, on which the LCIs here are based, used Ecoindicator 99, ReCiPe[80], and Cumulative Energy Demand as final impact categories, further frustrating the ability to compare between the results for different nanomaterials. Replicating the LCIs used previously and using only one impact assessment tool will allow for more effective comparison.

The USEtox method is chosen because of its focus on quantifying impacts to human health and ecotoxicity that result from chemical emissions. USEtox was developed under the Task Force on Toxic Impacts under the United Nations Environment Programme/ Society of Environmental Toxicologists and Chemists (UNEP/SETAC) Life Cycle Initiative [81]. Furthermore, USEtox is appealing because of its tractability in adapting chemical data into new characterization factors. USEtox develops characterization factors (CF's) that are used in impact assessment by quantifying

$$IS_t = \sum_i (CF_{ti} \times M_i)$$

where t is the impact category, in the present case freshwater aquatic ecotoxicity measured in cumulative toxic units (CTU_e). This unit, CTU_e, is itself used only in the context of USEtox, and is equivalent to PAFxm³xday where PAF is the potentially affected fraction of a species. M_i is the mass of chemical emitted to a specific environmental compartment, in the present case freshwater. Emissions data is taken from

the LCI gathered in the second step of LCA. USEtox quantifies the characterization factor as

$$CF = EF \times XF \times FF$$

where EF is the effect factor, XF is the exposure probability and FF is the fate factor.

The development of these factors is described in the text below Figure 3.3.

Given that LCIA characterization factors have not yet been developed for nanomaterials, necessary adjustments are made to the traditional USEtox method to develop interim characterization factors. Understanding the physicochemical properties is more important for nanomaterials than their bulk counterparts. Compounding this problem is the fact that these properties will change throughout the life cycle of the nanomaterial/particle based upon age and usage, these properties are often production or preparation method-specific, and the reference materials used in toxicology tests are not necessarily those that will occur in commerce. Given the degree and complex sources of uncertainty, the goal at present is not to resolve that uncertainty but rather to create the best possible estimates based on current knowledge and the variability therein.

To determine the most representative reference materials relevant for current needs and within current knowledge, scenario analysis is used to incorporate a wide range of release estimates and physicochemical properties. The scenarios consist of a) “no nano,” which represents previous studies that have left nanomaterial emissions and the direct toxicity of nanomaterials out of the impact assessment step, b) a “realistic” scenario, in which a broad range of scenarios are accounted for, and the median values are used, and c) a “worst case” scenario, in which the extreme values are used to demonstrate the possible uncertainty ranges given unlikely circumstances. These values

are physicochemical properties, toxicity results, and potential emissions scenarios, and are described further in the following sections. For each of the following factors, the USEtox model is adapted for each nanomaterial, necessary information for use with the model is taken from literature sources or substituted by experimental data for fate and exposure from literature as described below. The substance data tables used in these calculations can be found in Appendix C.

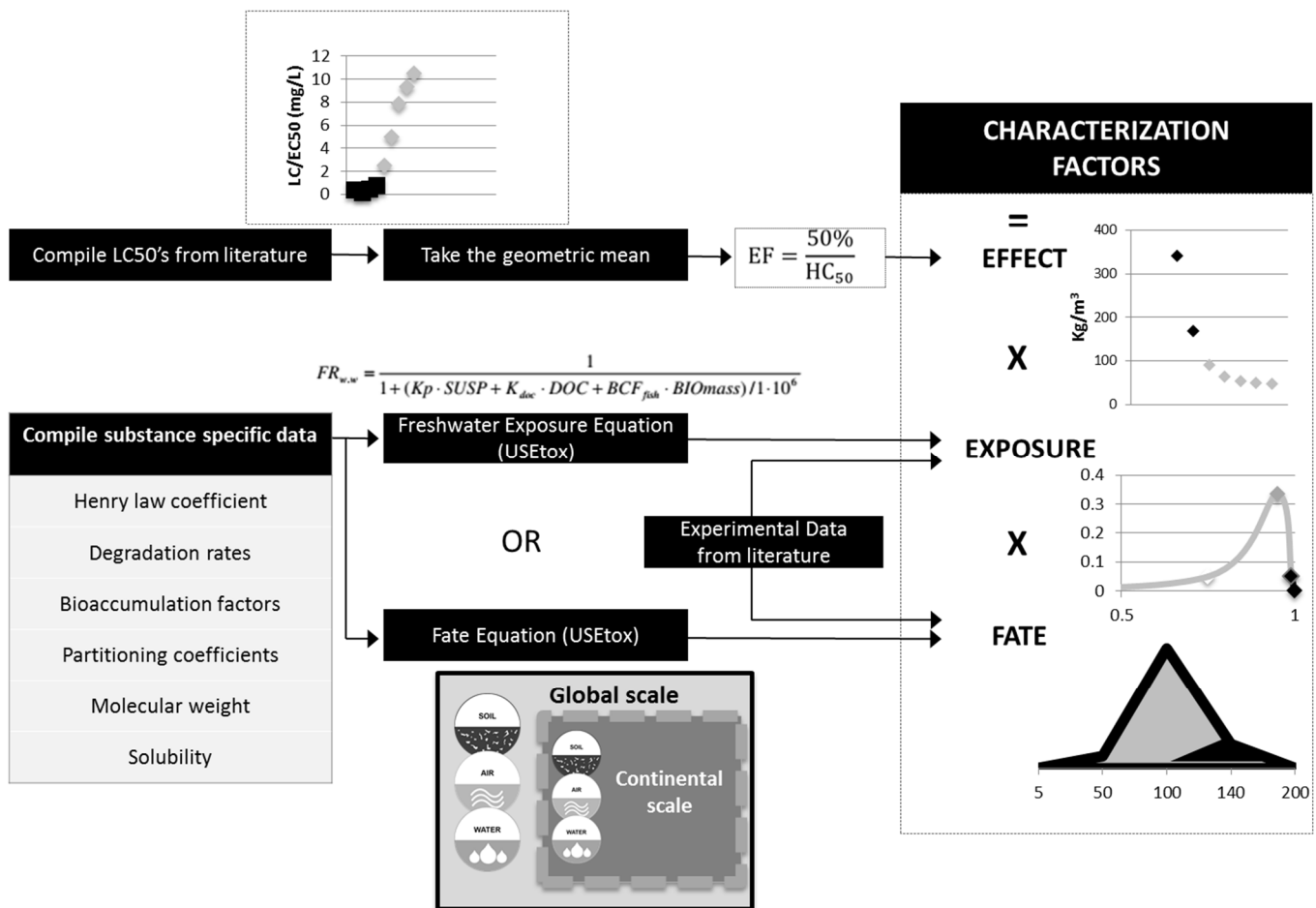


Figure 2.3 USEtox Method Theory and Adaptation. The method develops a range of fate, exposure, and effect factors using the USEtox method and ranges in physicochemical properties. In the graphs the black dots and shaded area represent the range of data used in the “worst case scenario” calculations, whereas the light gray represents the “realistic” ranges.

Effect The environmental toxicity from chemical emissions to freshwater are estimated by calculating the effect to at least three phyla: aquatic invertebrates, aquatic vertebrates and plants. USEtox calculates the effect factor from aquatic ecotoxicological data using measured LD₅₀/EC₅₀'s taken from literature, prioritizing measured LD₅₀'s from chronic mortality studies. The eco-effect factor is then calculated as $EF_{eco}=0.5/HC_{50}$ where the HC₅₀ is the geometric mean of all the species-specific LD₅₀'s. The LD₅₀'s differ based upon particle size, surface charge, surface coating, purity and other properties. Tables in Appendix A in the supplemental information summarize the LC₅₀'s used. The realistic EF_{eco} is based on the HC₅₀ derived from using the LC₅₀'s of all toxicology tests using all different types of nanomaterials (i.e. all sizes, surface coatings, etc.). The worst case scenario (WCS) EF_{eco} is based on the HC₅₀ derived from the most sensitive LC₅₀ found in literature. Much debate exists in the nano-risk community as to the proper way to model the contribution of ionic silver to nanosilver toxicity. The scenario approach here handles this issue, but improving assumptions about dissolution and ecotoxicity allocation are discussed further below.

Exposure The environmental **exposure** factor is the fraction of chemical dissolved in freshwater. Traditionally this would determine the probability that an aquatic organism will be exposed to the chemical. However, most of the studied case study materials are not likely to solubilize. Therefore, the exposure factor in the present case is interpreted as the “environmentally available fraction.” The best available information for partitioning coefficients between suspended solids and water, dissolved organic carbon and water, and the bioconcentration factor in fish, i.e. K_{pss} , K_{doc} , BCF_{fish} , respectively, are entered into the USEtox exposure equation. The data used is

summarized in Table C.1 in the Appendix. For the current study, the realistic and worst case scenarios are based on the data from [66] for SWNTs, C₆₀ fullerenes, TiO₂ results from literature, USEtox data, and other necessary assumptions for these three materials. These materials are not likely to dissolve readily, and so “the environmentally available fractions” will be close to 100% in both the realistic and the worst-case scenarios.

Fate The fate factor describes the duration that the nanomaterial will reside in the environmental compartment, i.e. freshwater, before degrading or partitioning into another compartment. The present study focuses on freshwater emissions at the concentrated level and residence time within this compartment. USEtox 1.2 [82] calculates the fate, measured in days, of a substance using substance-specific data. The data used is summarized in Table C.1 in the Appendix. Assumptions about fate are based on both the predicted values using substance data and measured values in a laboratory or actual freshwater, as reported in literature. NanoTiO₂ factors are based upon previous findings using a nested model [83]. Many of the substance-specific data required for the fate and exposure calculations can be revised continuously as better data becomes available.

2.3 Results

2.3.1 Toxic Potential: Characterization Factor Results

Characterization Factors (CFs) are calculated using the methods described in Section 2.2.3. Tables in Appendices A and C outline the data calculated and used in the calculation of realistic and worst case scenario characterization factors. In reference to ecotoxicity, many studies used multiple types of the same nanomaterial, and thus there

exist multiple LC₅₀ entries for some studies. As outlined above, a range of necessary data are taken from literature sources and applied to the USEtox model to yield a range of factors, from which the realistic and worst case scenario factors are then created. In terms of characterization factors, some materials demonstrate a large uncertainty in toxic potential. The calculated CF for nanosilver was over 250% greater than that reported by USEtox for ionic silver and over an order of magnitude greater than other traditional materials included in the USEtox model. Given that the current study finds such a large realistic CF, high volumes of nanomaterial emissions would be a cause for concern.

On the other hand, other nanomaterials do not show the same uncertainty. Carbon-based nanomaterials, C₆₀ and SWNT, due to the similarities in their modeling of fate and exposure, result in a similar *spread*, i.e. the difference between WCS and realistic CF's. However, the SWNT realistic CF is almost 250% larger than the C₆₀ realistic CF. Given these differences, using existing CFs based on the core material (e.g., carbon-based nanomaterial) in impact assessment involving nanomaterials is inadvisable. These results underscore that applying existing USEtox CFs for bulk materials in nanomaterial LCAs would yield unrealistic results. Conversely, the realistic value for TiO₂ falls much closer to the array of traditional USEtox metals, indicating that LCA of nano-TiO₂ could potentially treat the material as it would a bulk-size metal.

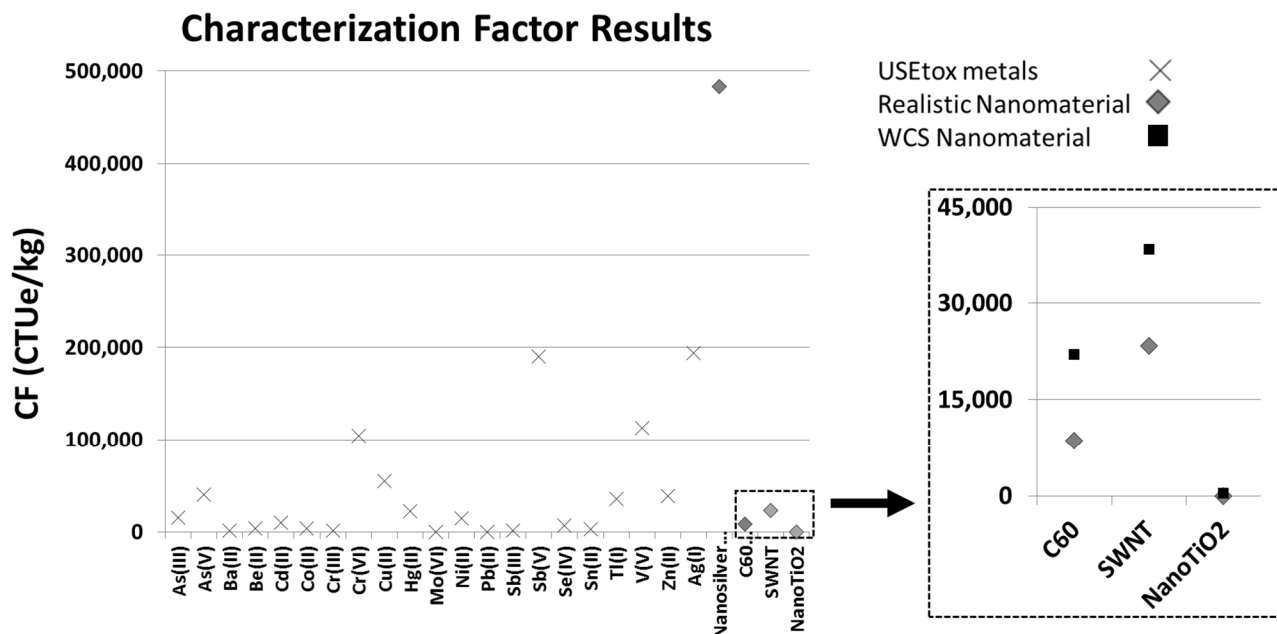


Figure 2.4. Characterization Factor Results: Figures demonstrate actual CFs for case study materials. The left graph depicts nanosilver in the two scenarios and compares it with the USEtox CFs for metals. The right hand graph depicts the three “insoluble” nanomaterials. The scales differ significantly in the two graphs.

2.3.2 Total Ecotoxicity Results

Primary drivers of ecotoxicity The following Figure 2.5 depicts the percent contribution to total ecotoxicity from four main sources: production electricity, embodied electricity, nanomaterial release, and “other.” The full ecotoxicity results are found in Appendix D. Production electricity is a measure of the electricity used directly in the production of nanomaterials. Embodied electricity is the cumulative electricity inputs in all upstream processes of material extraction and preparation. The results show that production electricity is the primary contributor to toxicity for SWNTs in all scenarios; production or embodied electricity is the primary driver of electricity in the no nano and realistic scenarios for C₆₀ fullerenes. Nanomaterial release is the primary driver of impact in the worst case scenario for all materials except SWNTs. These findings are consistent with a

previous analysis of [66], but are not representative of other nanomaterials. While results indicate that total electricity (production and embodied) typically plays an important role in total ecotoxicity for other materials, no clear trends have emerged that can predict the primary driver in all cases.

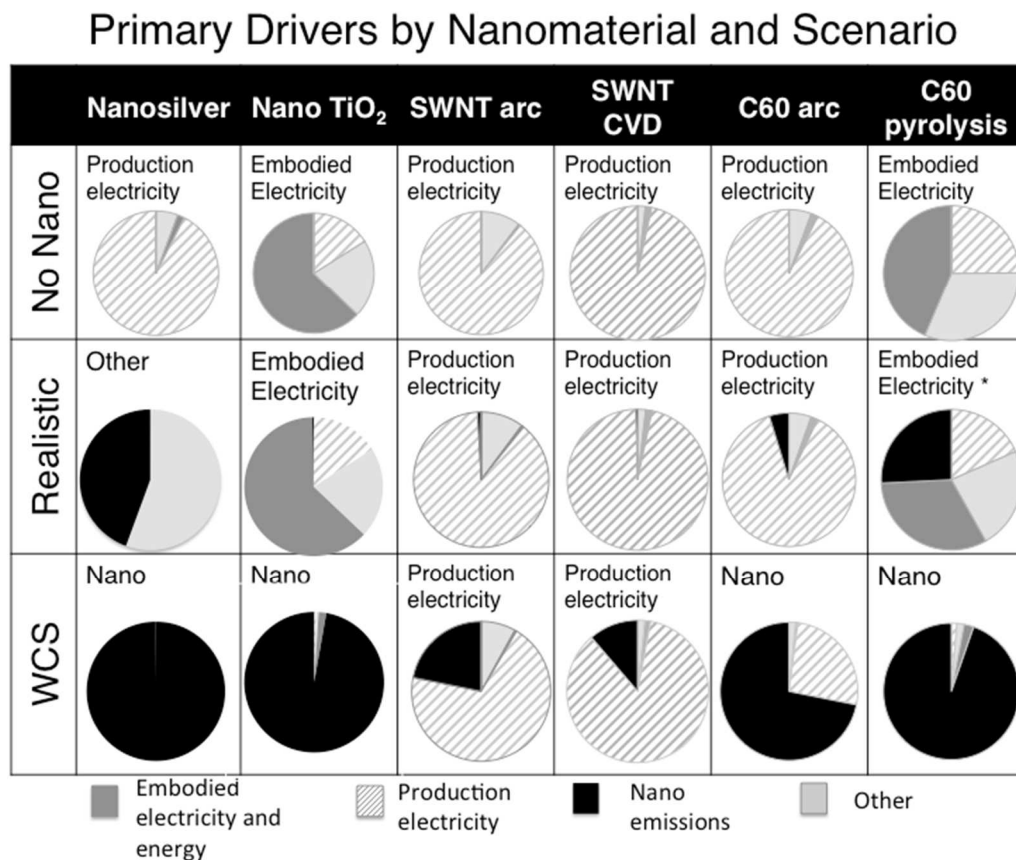


Figure 2.5. The Ecotoxicity Results by Percent Contribution for All Materials and in All Scenarios. *The primary drivers of ecotoxicity are written out.*

Production Methods: Contributions to total ecotoxicity impact do show consistency across production methods, although the number of similar production methods are limited. The production comparisons that are possible involve a) arc plasma for the two carbon based materials, i.e. C60 and SWNT and b) different types of pyrolysis, i.e. C60 and flame spray pyrolysis for nanosilver. The arc plasma methods are similar to each

other given that many of the inputs are the same and that carbon is the core material. Production of SWNTs requires a substantial amount of electricity, which is reflected in the present results. Figure 2.5 confirms that the percent contribution of production electricity to total impact is the same for SWNT and C₆₀; production electricity is the primary driver for SWNT and C₆₀ production by the arc methods. This would indicate that in realistic scenarios, production method may have more impact on final results than the actual toxicity of the nanomaterials, owing to the fact that nanomaterial ecotoxicity is relatively insignificant compared to embedded electricity and materials.

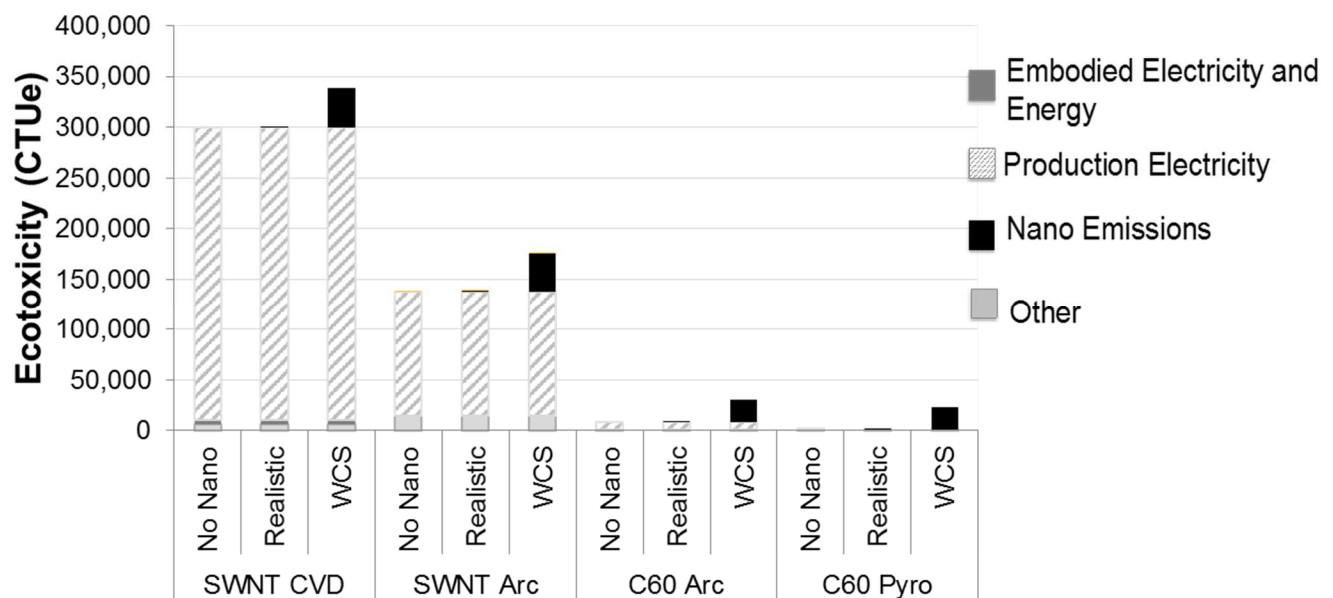


Figure 2.6. Ecotoxicity Results for Carbon-based Materials. *The ecotoxicity results for the carbon-based nanomaterials produced by alternate methods. The bar graph shows all three scenarios for both carbon-based materials.*

The results for nanosilver and C₆₀ produced by similar methods, i.e. pyrolysis, do not show the same similarity in percent contribution. The pyrolysis methods that produce C₆₀ and nanosilver differ more substantially due to the fact that the nanomaterials themselves are radically different. Because nanosilver exhibits a higher intrinsic toxicity, the realistic case is dominated by the nanomaterial release. The predominant contributor

to ecotoxicity in the nanosilver production method is overwhelmingly the mining and refining of the silver precursor, which is here depicted as “other.” Whereas the impact of C₆₀ production is driven by the electricity requirements more than material extraction or nanomaterial release in the realistic scenario.

Categories of Interest: Both core material and solubility have influence on the inherent toxicity of nanomaterials. In terms of ecotoxicity, the primary driver in all realistic cases of carbon-based nanomaterials is production electricity as demonstrated by the percent contribution graphs in Figure 2.5. However, in terms of the real value of ecotoxicity, there is a large discrepancy between SWNTs and C₆₀. The calculated SWNT ecotoxicity is on the order of $1-3 \times 10^5$ CTU_e, whereas the calculated C₆₀ ecotoxicity was $1-8 \times 10^3$ CTU_e. The drivers are the same for carbon-based materials, but the actual magnitude of total ecotoxicity diverge.

As with the characterization factor results, the ecotoxicity results show a stark difference between the insoluble nanomaterials and nanosilver. In the no nanomaterial release scenario, the nanosilver ecotoxicity is driven primarily by the mining impacts of silver (Figure D.2 in Appendix D), whereas material impacts are not influential drivers in the three other material cases.

2.3.3 Evaluating the Tradeoff Between Ecotoxicity and CED

In previous LCAs, cumulative energy demand (CED) has been found to be a good indicator of the total environmental burden [79] across multiple impact categories including ecotoxicity. The correlation between CED and ecotoxicity shows whether this

is true for nanomaterials and nanomaterial production. The findings thus far have indicated that in many realistic cases, i.e. carbon-based nanomaterials and nano-TiO₂, production, electricity is the primary driver of ecotoxicity, in others, the direct toxicity of nanomaterial release can dominate.

Cumulative energy demand (CED) is used as a proxy for electricity and energy demand. CED captures both the production electricity as well as the embodied electricity and energy for the entire life cycle or portion thereof modeled. CED is the cumulative energy required for the production per functional unit, accounting for all upstream material and energy inputs. The second metric to be captured is ecotoxicity. The intrinsic toxicity can be captured by proxy by either the Characterization Factors or the LC₅₀, i.e. the concentration at which 50% of the exposed population exhibits the adverse effect. These two metrics of course are related, and since both technically capture toxic potential of a material, both are used in the following comparisons. The following graphs show these results on a log-log scale.

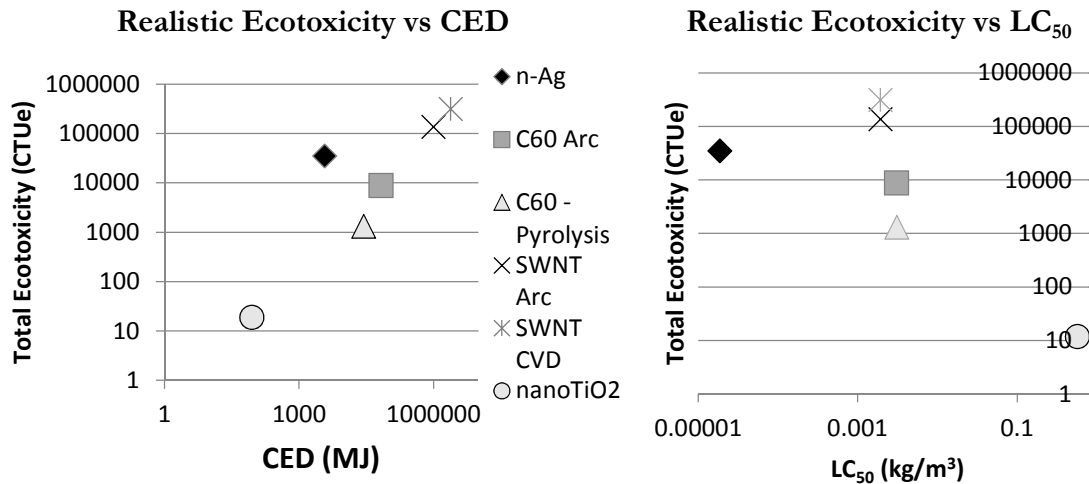


Figure 2.7 Correlation Results. Results displaying the graphs of total ecotoxicity, as calculated in section 2.3.2, versus the cumulative energy demand in the left graph and the LC₅₀ on the right.

	X	Y	With silver		No silver	
			Fit?	R ²	Fit?	R ²
Realistic	CF Realistic	Ecotox- Realistic	No fit	<0.02	Linear	0.75
	LC ₅₀ Realistic	Ecotox- Realistic	Linear	0.11	Linear	0.14
	CED	Ecotox- Realistic	Linear	0.99	Linear	>0.99
Worst Case (CF)	CF WCS	Ecotox- WCS	Linear	0.76	Linear	0.61
	LC ₅₀ WCS	Ecotox- WCS	Linear	0.52	Linear	0.60
	CED	Ecotox- WCS	Linear	0.05	Linear	>0.99

Table 2.1 Correlation Results. *The table displays the R² values of a linear regression between total ecotoxicity and the three metrics representing energy demand (CED), intrinsic toxicity (LC₅₀) and toxic potential (CF).*

Results show that materials with high CED have an overall higher total ecotoxicity. The outlier in this graph is nanosilver, which was found to be more intrinsically toxic in section 2.3.1. Because nanosilver is more toxic than the other case materials, nanomaterial emissions play more of a role than that of direct and embodied energy inputs. The materials that do follow the trend shown here are those that are considered insoluble in freshwater, and while they do exhibit some toxicity as particulate, the contribution is less than that of the total energy demand. Additionally, Figure 2.7 shows that with decreasing LC₅₀, ecotoxicity increases. This would mean that for those nanomaterials with a smaller LC₅₀, i.e. more intrinsically toxic, the overall ecotoxicity impact was larger and at a rate more steep than with CED.

Table 2.1 displays the results of a simple linear regression between the drivers, i.e. intrinsic toxicity and energy demand, to demonstrate which metrics are related. The columns labeled “with silver” and “without silver” refer to the inclusion of the nanosilver data points in the data regression given that silver has been an outlier throughout the results of this study. The regression shows a strong relationship between CED and the

realistic ecotoxicity results when run with and without silver. Furthermore, there is a strong relationship between the CED and worst case scenario ecotoxicity results when silver is excluded, presumably because the ecotoxicity results are dominated by nanosilver toxicity in this scenario. Though visually there seemed to be a correlation in LC_{50} versus ecotoxicity, the regression results do not support a strong trend. In both realistic and worst case scenarios, the correlation between CF and Ecotoxicity changes very little when nanosilver is included and excluded, indicating that nanosilver toxicity actually falls in line with the other nanomaterials' toxicity. Rather, the fate and exposure of nanosilver, which are included in the CF but not the LC_{50} , are the most significant factors in indicating total ecotoxicity.

While it is expected that the proxies for inherent toxicity, CF and LC_{50} , would show similar correlations, these proxies do not correlate in the same circumstances. Because of the divergence, it is apparent that the fate and exposure factors also play a vital role in determining the toxic potential, and therefore toxicity should not be captured entirely by the LC_{50} metric.

Last, when silver is excluded from the regression, both realistic and worst case scenarios CFs show some correlation with overall ecotoxicity, but these correlations are less compelling than those reported for CED, indicating that CED is overall the best proxy for total ecotoxicity in the case of the three insoluble nanomaterials.

2.3.4 Using Nanomaterial Toxicity Characteristics to Forecast Policies

Nanomaterials are similar only in dimensionality, not in fate, toxicity, or the methods by which they are produced. While it is true that upstream electricity production and direct electricity production are significant for many of the nanomaterials discussed, the case of nanosilver begs the question are there scenarios in which regulation is not addressing the potential risks of nanomaterials?

As demonstrated by the differences between CNTs and nanosilver, the impacts that nanomaterial emissions produce differ depending upon the type of nanomaterial. Furthermore, the product will become important as the nanoparticle itself and use will determine at which life cycle stage exposure potential is most probable. Therefore, it is necessary to develop a paradigm outlining the potential for regulation to reduce ecotoxicity. The following paradigm in Figure 2.8 ties regulation to the important parameters from environmental and human health toxicity impact assessment. The levels of regulation are determined as follows: a) Low means that regulation handles the ecotoxicity risk *or* that there is little potential for further regulation in this space b) Medium may mean that it is dependent upon the nanomaterial or product, no generalization can be made c) High means that there is potential for nanomaterials ecotoxicity risk to manifest into a policy-related problem.

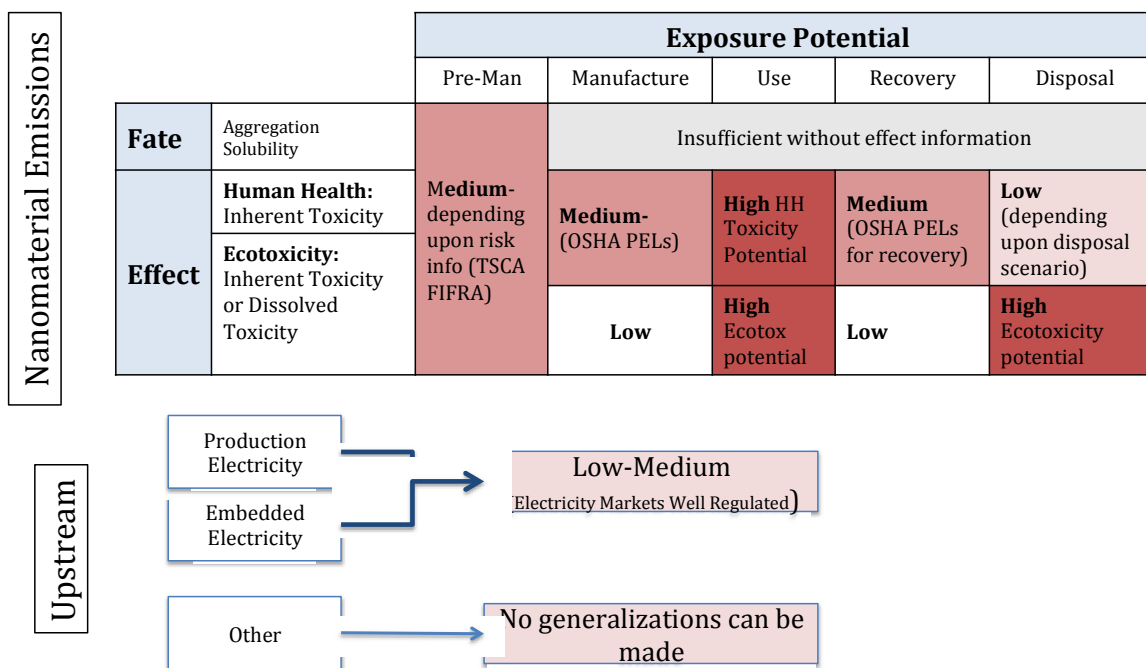


Figure 2.8 Paradigm for Projecting Regulations for Nanomaterials. *The table contains information on how to regulate nanomaterial emissions. Given that exposure potential is expected to be high for a given life cycle stage, i.e. pre-manufacture, manufacture, use, recovery or disposal, one can expect a high, medium or low risk depending upon whether aggregation, solubility, or inherent toxicity are also relatively high. If, however, production or embedded electricity are the driving source of environmental impact, then there is a low or medium potential for regulation to step in.*

Results

The table contains information on how to regulate nanomaterial emissions for any given nanomaterial in any given product. When exposure potential is expected to be highest for a given life cycle stage, i.e. pre-manufacture, manufacture, use, recovery or disposal, the table tells where there is a high, medium or low potential for new regulation to be introduced or increase stringency to accomplish risk reduction. This of course also depends upon the identified nanomaterial characteristics identified, i.e. aggregation, solubility, and inherent toxicity. If, however, production or embodied electricity are the driving source of environmental impact, then there is a low or medium potential for *new*

regulation to be introduced and reduce environmental impact substantially. To demonstrate the utility of the paradigm, consider two types of products: consumer products where use exposure potential is high and cases where occupational exposure are expected.

Use

Many consumer products have potential consumer exposures and fewer protections. The Consumer Product's Safety Act (CPSA) [84] and the Federal Food and Drug Administration (FDA) have investigated the use of nanomaterials in products where consumer exposure potential is high by doing risk assessments similar to those in TSCA and other supplemental exposure and toxicity assessments. As yet no nanomaterials have been banned from consumer products and so no mandatory regulations are in place in the US. In contrast, the French government has imposed mandatory labeling of nanomaterials in skincare products.

Despite the fact that none have yet been outright banned, the important factors identified here, inherent toxicity and solubility, could be useful for prioritizing future risk assessments. Figure 2.9 depicts three of the case study nanomaterials and the life cycle stage where probability of exposure will occur for current consumer products listed in the Consumer Products Inventory.

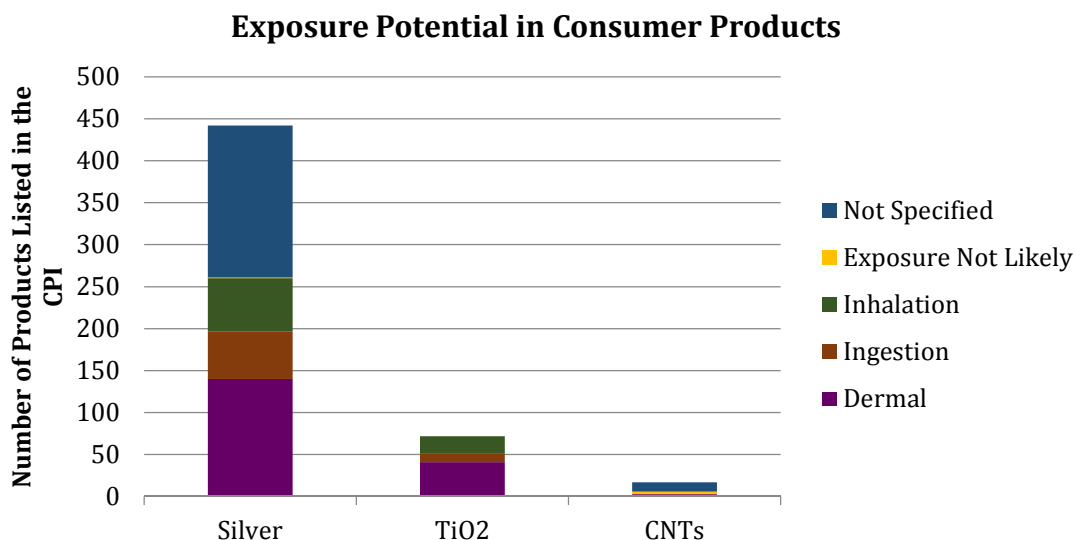


Figure 2.9 Number of Nanoproducts in the Consumer Products Inventory and the Pathway Through Which Exposure is Expected

Future efforts that affect consumer products in the US will likely be soft-law regulations that help the public understand the risks of nanomaterials. Very briefly these could be things such as public information campaigns, information clearinghouses about the presence of nanomaterials in products and the best available research on risk, eco-labeling, standardizing nano-classifications under initiatives such as the EU’s ecolabels, and acquiring unbiased risk information through reporting programs. These would be relevant for those products with which the consumer will likely be exposed during use such as skin products, children’s products, textiles, and food and beverage containers.

Occupational Exposure OSHA PELs limit the amount of potentially harmful material that a worker can legally be exposed to over an eight-hour workday, with specifics on exposure pathway, measurement techniques, and personal protective equipment [85]. Nanomaterials could be regulated by the PEL of their corresponding bulk materials or as “particulates not otherwise regulated.” Figure 2.10 graphs OSHA

PELS and NIOSH RELs (Recommended Exposure Limits), those limits that are not mandatory but are recommended for a safe workplace, for particulates and fibers from in the National Institute for Occupational Safety and Health (NIOSH) Pocket Guide to Chemical Hazards.

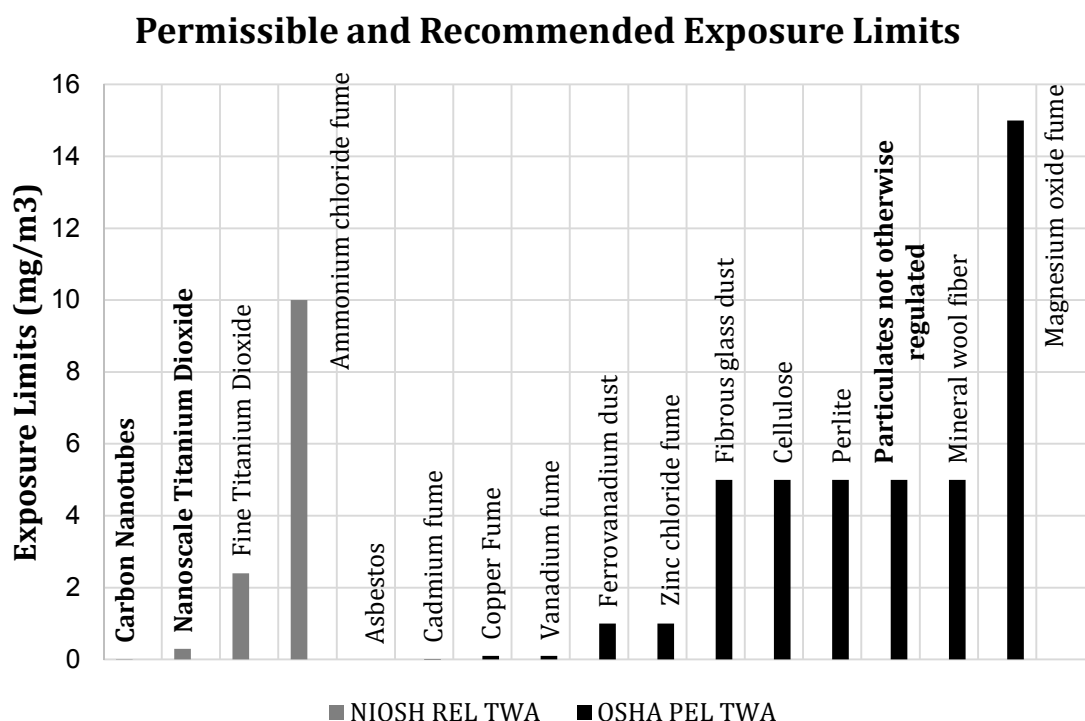


Figure 2.10 Permissible and Recommend Exposure Limits for Particulates, Fumes and Fibers

Figure 2.10 demonstrates that nanomaterials require their own, more restrictive, exposure limits given the difference between safe exposure levels for fine titanium dioxide and nanoscale titanium dioxide. Furthermore, the current default exposure limit, the PEL for “particulate not otherwise regulated,” will not be strict enough for nanomaterial exposure. Some of the important characteristics for “Particulates Not Otherwise Regulated” PEL (pathway, impact, etc.) are relevant for nanomaterials, but this PEL is not stringent enough for some nanomaterials.

NIOSH recommended exposure limits (RELs) and the corresponding personal protective equipment are based on a thorough review of medical, biological, engineering, trade and other scientific literatures and undergo a commentary period [85]. NIOSH has set the REL for CNTs at $1 \mu\text{g}/\text{m}^3$ as an 8-hr TWA [86], a REL for nanoscale TiO_2 at $0.3 \text{ mg}/\text{m}^3$, significantly lower than the OSHA PEL for bulk-sized TiO_2 at $15 \text{ mg}/\text{m}^3$ [87]. No further PELs or NIOSH guidance are available for other nanomaterials. Given that new PELs are established infrequently, about once every five years, it is unlikely that this mechanism will be available in the near future for the wide diversity of nanomaterials produced and the rapid developments in nanotechnology.

There is potential for a predictive exposure limits given control banding. Control banding is a type of decision analysis method, which predicts exposure limits control measures with identifiable hazards and exposure probabilities to apply the best known risk-reducing strategies at a certain stringency level [88]. Hazard banding techniques can establish occupational exposure “bands” (OEBs) for a greater number of chemical hazards with a smaller amount of information [89]. Proactive manufacturers can use these OELs and other safety precautions suggested by NIOSH to protect their workers. Besides the benefits of having a safer work place, using these precautions may prevent liability in the future when greater risk information is established and workers recognize that their exposure to nanomaterials may have caused an adverse physical effect.

2.4 Discussion and Future Work

Depending upon the specific nanomaterial impact, fate and exposure probability, the omission of direct nanomaterial impact can be significant to the outcome of an LCA

for a nano-enabled product. The characterization factors calculated here using literature data and modeled on the USEtox method for the case study nanomaterials found a significant difference between the two scenarios for both carbon-based materials. The difference between nanosilver scenarios was the most significant. The exception to this trend was that nano-TiO₂, which had a much smaller CF, falling on the order of traditional USEtox metals.

In Section 2.3.2 production and embodied electricity were found to be the primary drivers for the carbon-based materials and titanium dioxide. Whereas a previous study[66] found that electricity production was the only significant source of ecotoxicity impact, this study found that the influence of electricity production to be much smaller. However, comparing energy demand and total ecotoxicity verified that there is a correlation between increasing energy demand and total ecotoxicity. The ecotoxicity results also showed the differences between materials by demonstrating that for some materials, i.e. nanosilver, the impact of mining input materials is a more significant driver than electricity production.

Given that the models for impact assessment were adapted here specifically for case study materials, there is potential for further adjustment to the USEtox or other LCIA ecotoxicity methods to take into account the nonlinear nature of the dose-response curve. USEtox models the effect factor on the LC₅₀, a single number on a nonlinear curve, and so as emissions of a material increase, the total impact increases linearly. Furthermore, not all dose-response curves follow the shape, as assumed in USEtox. Impact assessment tools here were altered to incorporate the unique considerations of each material and that this type of work will be necessary in the near future for those

wishing to perform nanomaterial LCA. This type of specificity and scenario approach used here which takes into account a wide range of potential LC₅₀'s and substance-specific data points could be used for traditional materials with atypical dose-response behaviors.

One of the significant challenges encountered here was choosing the correct parameters for nanosilver given its partial solubility. This property was found to be the most influential in separating the case studies. Furthermore, the solubility of nanosilver contributes to the overall toxicity due to the fact that ionic silver is inherently toxic. More complex modeling work will be necessary to better model the dissolution and isolate nanosilver toxicity from ionic silver. Further, future life cycle assessments involving nanosilver should carefully measure or model the nanomaterial emissions since these emissions were shown to contribute a significant percent of the total toxicity. Modeling other partially soluble nanomaterials could determine whether toxicity or solubility determines the overall drivers of ecotoxicity.

These results focus on ecotoxicity produced on a per kilogram basis but will enable future, fuller LCAs of product containing these case study nanomaterials. Because these impacts can be put in context of potential benefits to weigh the potential risks and benefits, future work will look at the broader context of the increasing demand for nanomaterials. Given that the CED is potentially useful proxy for the ecotoxicity of nanomaterial production, these impacts should not be ignored when performing future LCAs and making ecological risk-related regulatory decisions. Future work will look at the emissions and impacts in a regulatory framework to identify whether these impacts are currently being contained and where these impacts will occur.

CHAPTER 3. Regulating Nano-enabled Products: Implications for energy storage technologies

3.1 Introduction

As discussed in the introduction, engineered nanomaterials (ENMs) are or will be used in consumer products, medicinal applications[4], environmental remediation [90], [91] and as coatings, catalysts, or simply to replace bulk versions of the material; the benefits they afford are extensive and include improved strength, radiation-blocking, enhanced efficiency, durability, and anti-bacterial and anti-microbial qualities [15]. Given these benefits, it is not surprising that the number of applications for nanomaterials is growing rapidly and that their uses span many product and industrial sectors.

Sector	2010	2011	2012	2013	2014	2018
Materials and manufacturing	\$198	\$306	\$435	\$599	\$799	\$1,755
Electronics and IT	\$101	\$149	\$211	\$298	\$414	\$940
Health care and life sciences	\$35	\$51	\$71	\$98	\$133	\$384
Energy and environment	\$5	\$8	\$13	\$19	\$28	\$89
Total	\$339	\$514	\$730	\$1,014	\$1,375	\$3,167

Table 3.1 Global revenue in million US Dollars from nano-enabled products by sector. *Up to 2012 is historical data [92] and data points after 2012 are projections by constant growth rate.*

While the benefits of nanomaterials are well characterized, the potential emerging environmental risks of nanomaterials themselves are not as well documented. Whereas Chapter 2 showed that the inherent toxicity of nanomaterials are not significant when compared to the electricity inputs in most cases, these results were on a per kilogram basis. Given the significant growth in this sector, the inherent toxicity of nanomaterials

as well as the electricity requirements could raise cause for concern as national and global production volumes begin to explode without anticipatory governance.

Determining the environmental risk of nanomaterials consists of synthesizing the probability of exposure with the probability that exposure will produce an adverse impact to human and/or environmental health. Currently, risk assessment suffers from a lack of sufficient understanding about a) how nanotechnology is being used by manufacturers, b) the probability of exposure, and c) potential effects nanoparticles could produce at a very general level. This challenge is exacerbated by the different time scales of commercialization and regulation. The development and availability of nano-enabled products is fast, dynamic, and funded. Conversely, environmental health and safety research is not given the same attention. Adequate regulation cannot be implemented without a demonstrable risk. These challenges create a daunting task for policymakers and regulators leading to an often-fragmented risk management approach for nanotechnology.

3.1.1 Case Study Motivation

To address these issues of significant growth in an industry without proper methods for risk reduction, a case study in the energy materials sector is chosen to demonstrate the potential risks and gaps in regulation. A large proportion of nanomaterials go into applications into the energy materials sector and the economic value of the final products is significant, as demonstrated by Table 3.1. Included in this broad category are applications in energy generation, storage and delivery. Nanomaterials produced for energy materials have grown considerably in recent years

and are projected to experience annual revenue increases of 20- 30% in the near future, as shown in Table 3.1. In the energy sector, nanomaterials are used or will be used in lithium ion batteries, photovoltaic cells for producing solar power, wind turbine blades for wind energy generation, and fuel cells. The functions of nanomaterials in energy materials are varied: increasing battery capabilities, dematerialization, materials strengthening. The nanomaterials that will enhance the performance of photovoltaic cells used for producing solar energy are titanium dioxide nanoparticles in dye-sensitized cells, fullerenes in organic photovoltaics, nanoscale silicon, CIGS or silver in thin film solar photovoltaics, and quantum dots in next-generation modules [93] [94]. Wind turbine blades will be improved in their vibration damping, hydrophobicity and friction resistance with the addition of carbon nanofibers [95] and nanoscale glass fibers [96].

One important nanomaterial in the energy materials sector is the case of lithium-ion batteries, which are used to store and deliver energy for a myriad of growing applications: consumer electronics, laptop computers, electric vehicles, and battery technologies for renewable energy generation. Future generations of lithium ion batteries may contain carbon-based nanomaterials such as nanotubes, silicon nanotubes, iron phosphates and others [5]. Improvements to lithium ion batteries from the use of nanomaterials include weight reduction, increased lifespan and increased energy density, which are critical needs for the future of electric vehicles and storage of energy produced by renewable sources. The production of CNTs for these batteries will increase, which will have two competing impacts on the environment. On one hand, increased production of CNTs will adversely impact the environment by increasing the demand for the materials and electricity required for production and the emissions of CNTs into the

environment. On the other hand, improvements in energy storage will enable many renewable energy technologies, resulting in a positive environmental impact by displacing traditional energy production methods. The present analysis intends to assess and recommend policy directions for reducing the unintended environmental consequences of nanomaterial production and disposal. Use is excluded from the analysis since CNT emissions are predicted to be small [12, 97] during this stage and because Chapter 2 showed that direct emissions contribute a comparatively small impact.

Carbon-based nanomaterials are the most commonly produced nanomaterial both globally and domestically. This category includes graphene, carbon nanotubes, and fullerenes, C_{60} or C_{70} [98]. Market reports, governmental organizations, and academic studies [1] estimated global production to be anywhere from 50 tons per year to 3000 megatons per year in 2011. The CNT market represents over a 100 billion USD market, and approximately 50% of the global production of CNT[99] occurs in the US. With such a large discrepancy between CNT production estimates, there is clearly need for better discussion about the drivers of demand for CNTs, the possible unintended consequences of increased production and the potential risks.

In order to better assess the production of carbon nanotubes and the environmental impact thereof, carbon nanotubes in lithium ion batteries are chosen as the case study by forecasting the technologies that will use lithium batteries, modeling the corresponding increase in Li-ion battery cell production, forecasting CNT production for these cells and then assessing the environmental fate and impact of these CNTs once released from the battery cell. Last, the paper contains an exploration of the current policy environment as it relates to nano-containing products and recommendations for

reducing potential risks of both CNTs in batteries and other uses of nanomaterials in the energy materials sector.

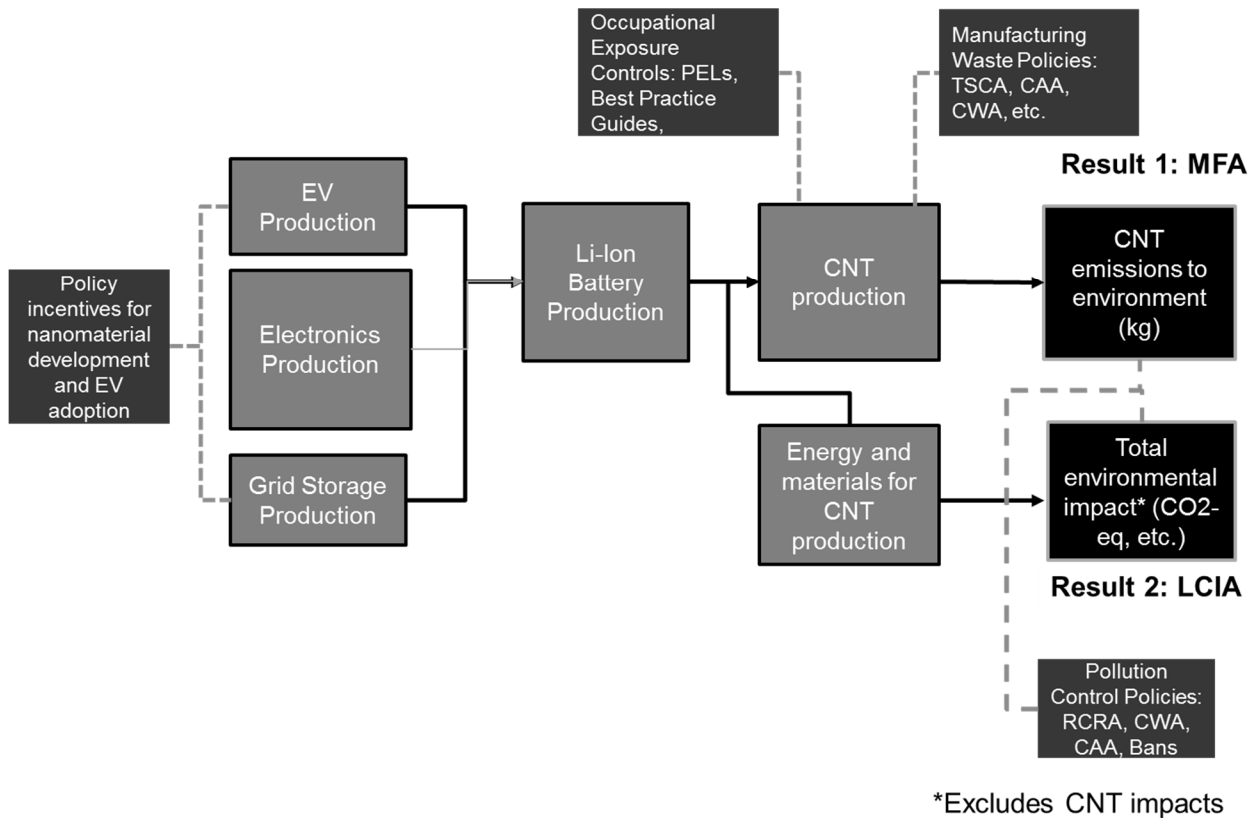


Figure 3.1 Scope of Chapter 3 Analysis. *The production of CNTs for Li Ion Batteries is forecasted by first looking at forecasts for the major technologies that will use these batteries. There are three results: CNT production and emissions to the environment, the total environmental impact of CNT production and the role of policy throughout the scope. Policies relevant to the scope of the study are briefly outlined in dark gray.*

The myriad of challenges in nano-risk assessment creates difficulty for decision makers who must act without the necessary information. Meanwhile, nanoproducts are increasingly introduced into commerce without mechanisms in place to reduce risk to workers, consumers or the environment as a whole. It is important to keep developing these gaps and develop appropriate regulations to protect human and environmental health.

3.2 Methods

3.2.1 Case Study Method: Material Flow Analysis

Material flow analysis is used to forecast the future production of carbon nanotubes for lithium ion batteries. Material flow analyses have proven a useful tool for informing policy-makers on the impact of goods and services like electronics [100] [101] fuels like nuclear [102], biomass [103] and other energy materials [104], [105, 106] . Material Flow Analysis (MFA) quantifies the flows of materials between different systems and the stocks of the material in these systems over time. Determining the stocks and flows of materials enables exposure assessment by describing the routes and quantities that enter the environment. This case study analysis will forecast the flows of carbon nanotubes used in energy storage by extrapolating from the growth in key technologies.

The stock and sales of three of the important technology sectors are forecasted using the logistic curve. The logistic curve has been used for population growth in ecology and is here used to model technological growth and penetration. The equation relates the penetration rate $N_i = \text{stock}_i / \text{population}_i$, the intrinsic growth rate, r , and the carrying capacity, K . The carrying capacities used here are determined by imposing a physical limit to the stock of the technology, as described in Table 3.4. Then, using the following equations and recent actual sales and stock of these technologies, the intrinsic growth rate is optimized by reducing the least squares difference between the Actual penetration rate to the forecasted penetration rate. The physical limits, carrying capacities, and intrinsic growth rates used are found in Table 3.4.

$$N_i = \frac{K}{e^{-(ri+C)} + 1}$$

$$N_i = \frac{stock_i}{population_i}$$

$$C = \ln\left[\frac{N_0}{K - N_0}\right]$$

In the case of electronics, assumptions from previous studies and U.S. EPA data are used to model electronics production as a logistic curve. The logistic method is also used for energy storage forecasting and fit using 2001-2015 electrochemical storage systems data from the Department of Energy's Global Energy Storage Database (GESD). For electric vehicles, the U.S. EIA forecasts of electric vehicle, plug-in hybrid and hybrid electric vehicle sales are used for the entire timespan of this analysis.

The method tracks the stock of material in use in time period i , $Stock_i$, those being brought into use, $Sales_i$ and those being retired, i.e. the outflows, in time period i , O_i . The outflows are those that were sold in time $i-lifespan$, the lifespan being the assumed timespan that the technology is used.

$$Stock_i = Stock_{i-1} + Sales_i - O_i \quad (Eq\ 1)$$

The flows of carbon nanotubes are the result of their use in lithium ion batteries, and so this calculation estimates the flows of lithium ion batteries for electric vehicles, mobile devices, laptop computers and storage for grid load leveling. Equation 1 then becomes

$$Stock(C)_i = \sum_{t_n} c(t_n)_{i-1} * Stock(t_n)_{i-1} + c(t_n)_i * Sales(t_n)_i \\ - c(t_n)_i * O(t_n)_i \quad (Eq\ 2)$$

which relates the stock of carbon nanotubes at time i with the sum, over each technology t_n that uses LiBs, the sales of that technology and the outflows $O(t)$, each multiplied by the CNT intensity of each technology $c(t)$.

Last, these forecasts are made in two scenarios: baseline and aggressive. The aggressive scenario predicts a more aggressive growth in technology and use of carbon nanotubes in LiBs in order to estimate the maximum potential for exposure and environmental emissions of CNTs in this sector. In this way, the forecast can predict the maximum possible environmental impact in order to determine whether regulation will be adequate in any scenario.

Electric Vehicles

The U.S. Energy Information Administration (EIA) forecasts plug-in hybrid (PHEV), hybrid (HEV) and battery electric vehicles (BEV) sales to the year 2040 with three potential growth scenarios[107]. A graphical depiction of EIA sales projections and stock (calculated from EIA sales data and *equation 1*) can be found in Figures 3.3 and 3.4. While previous EV studies have assumed lifespans as low as 5 years, the US Department of Energy predicts battery lifespan to increase to 8-10 years in the near future [105]. At the end of use in an electric vehicles, these batteries will still retain 80% of original charge capacity [108], thereby increasing their useful life past their primary use. The average battery mass for each type of alternative vehicle was calculated using the BaTPaC tool [109]; the assumptions about battery size in kilograms are found in the following table, and is based upon the average number of cells from and a bill of materials generated from BaTPaC are summarized in the following table (3.3).

Scenario	Cathode Chemistry	Vehicle Type			
		BEV	PHEV10	PHEV40	HEV
Baseline	LiCoO ₂	230	26	106	31
	LiMn ₂ O ₄	264	30	121	36
	LiFePO ₄	275	31	123	38
	Li(NiMnCo)O ₂	194	22	89	27
	Average	241	27	110	33
Aggressive	LiCoO ₂	299	35	138	46
	LiMn ₂ O ₄	344	40	156	54
	LiFePO ₄	360	41	165	59
	Li(NiMnCo)O ₂	257	30	118	41
	Average	315	37	144	50

Table 3.2 EV Battery Size (kg) by Cathode Chemistry and Vehicle Type

Electronics and Laptops

Previous forecasts have modeled growth in electronics and laptops using the logistic function, used in ecology, economics, medicine and diverse scientific fields. The shape of the curve portrays the rapid initial growth of technology adoption and slowing as the population becomes saturated with electronic devices at some optimal penetration. The present analysis uses the US Census Bureau’s forecasts for population growth [110] and the US EPA’s data for personal electronics and laptops[111]. The initial data used for personal electronics, which is intentionally vague, included cellular devices, PDAs, and while the laptops category included only portable computers. The landscape of personal electronics is difficult to changing as PDAs are no longer used and manufactured, while other types of personal electronics are increasingly common. For this reason the secondary category is here defined as “personal electronics” in order to keep the category vague to account for future products.

The average lifespan of these devices has decreased as laptops and personal electronics technology has matured [112]. Therefore, a conservative lifespan of 3 years is used in the baseline, following [100] and [113]. Similarly the EPA document assumes between 2-10 years for cellular phones with the majority (over 60%) being disposed of at 2 years. Thus, the baseline assumptions here are 3 years for laptops and 2 years for mobile devices, decreasing to 2 years and 1.5 years, respectively, in the aggressive scenario. While this average lifespan may be too short for current devices, it will likely be conservative as the technologies advance.

Energy Storage Applications

Significant growth is expected in the use of lithium ion batteries for electrical energy storage, which is used for peak load leveling, renewable energy production storage and other stationary energy storage. Among batteries in this application, LiBs make up approximately 50% [114], but industry sources predict LiBs to make up 70% of newly deployed systems in 2014 [115] and growing to up to 90% of deployed EES by 2025. The present analysis relies upon these estimates and assumes steady growth from 50%-70% from 2015 to 2035 for newly deployed electrochemical energy systems are LiBs, while the sensitivity analysis assumes growth from 50- to 90%. The amount of deployed electrochemical EES deployed nationally is taken from data in the Global Energy Storage Database (GESD) [116].

Future forecasts are made based upon the GESD database fit with the logistic function. Typically LiB lifespan is dependent upon cycles, which may vary depending upon the usage, but for the present purpose a lifespan a range between 8-15 years [117] is

used. The specific power of LiBs is assumed to be 250 W/kg and varied between 200-300 W/kg [118] in the sensitivity analysis. Because there has been little previous modeling of “carrying capacity” for lithium ion batteries in EES, a range of values are used which represent a maximum EES deployment equivalent to an up to 20% portion of the electrical grid in the year 2040. Defining the carrying capacity in this way indicates that the EES stock is growing *toward* 20% of the electrical grid, not necessarily reaching it by the year 2040. Again the intrinsic growth rate, r , was optimized to the in both baseline and aggressive scenarios by minimizing the least squares difference between projected penetration and actual penetration.

Technology	Scenarios	Lifespan (years)	Mass of Battery	Growth scenarios	Alternative vehicle sales:
Electric Vehicles	CURRENT	5-10 years	45-142 kg [109]	--	16% of total vehicle sales
	BASELINE	10 years [105]	45-142 kg [109]	Reference EIA forecast [107]	17.8% [107]
	AGGRESSIVE	5 years [105]	45-142 kg [109]	Maximum of all three EIA forecast scenarios [107]	17.8% [107]
Mobile Devices/Small Personal Electronics	CURRENT		34.9-41.7 g/cell [119]	Logistic growth forecast fit to EPA data [111] and carrying capacity	Maximum Penetration Rate (carrying capacity)
					1.45 devices/person in 2010
	BASELINE	2 years [111]	34.9 g		2 devices/person
	AGGRESSIVE	1.5 [111]	41.7 g		4 devices/person
Laptops	CURRENT				0.39 devices/person in 2010 ([113])
	BASELINE	3 years [111]	131 g [120]		0.63 devices/person [113]
	AGGRESSIVE	2 years [111]	150 g [113]		0.9 devices/person in [113]
Energy Storage	CURRENT	10-15 years [117]	Specific Power 200-300 W/kg [118]	Logistic growth based upon GESD data [116] and 4-	9.02E-10 GW/person

	BASELINE	10 years	250 W/kg	12% of grid production	9.86E-08 GW/person. Corresponds to 4% of grid production
	AGGRESSIVE	9 years	200 W/kg		3.64E-07 GW/person. Corresponding to 12% grid production

Table 3.3 Baseline and aggressive assumptions used for the values necessary for making technology forecasts

Carbon Nanotube Intensity

While CNTs may replace active battery materials in the future, they are likely used now as a conductive additive in the battery anode though there is little information to show how much. Carbon intensity of each technology, i.e. mass CNT/battery for each technology, is extrapolated from scientific literature and expert opinion. Between 1-2% by weight of the active material has been estimated to be a carbon-based nanomaterial previously [113]; however, this would increase the cost of batteries dramatically given that current price of LiBs and CNTs. Here a 0.1% estimate is used in the baseline and raised to 1% in the aggressive scenario. The mass of each battery by technology type is taken from previous MFA [105], retail sources of mobile batteries [119] and the BaTPaC tool for EV batteries [109]. It is also assumed that only a portion of all Lithium ion batteries contain CNTs, varying this amount between 10% in 2015 to 75% in 2040 in the baseline case[113]. This rate, the CNT penetration in the LiB market, and the change in this number is demonstrated in Figure 3.2.

	CURRENT	BASELINE	AGGRESSIVE
CNT Use Per Battery	0%	0.1% active anode material weight	1% battery weight
Penetration of CNT-enabled into Market	0% batteries use CNTs	Increased from 10-75% from 2010-2040	Increased from 50-99% from 2015-2040
Anode Size	30% anode/battery by mass	30% anode/battery by mass	N/A (Battery assumptions based on total battery weight)
LiB penetration (% of technology using LiBs)	50% HEVs using in 2015	50% to 75% in 2020 [103], constant growth thereafter	50-100% by 2020

Table 3.4 CNT Assumptions Used in Calculating Future Flows of CNTs for LiB Production.

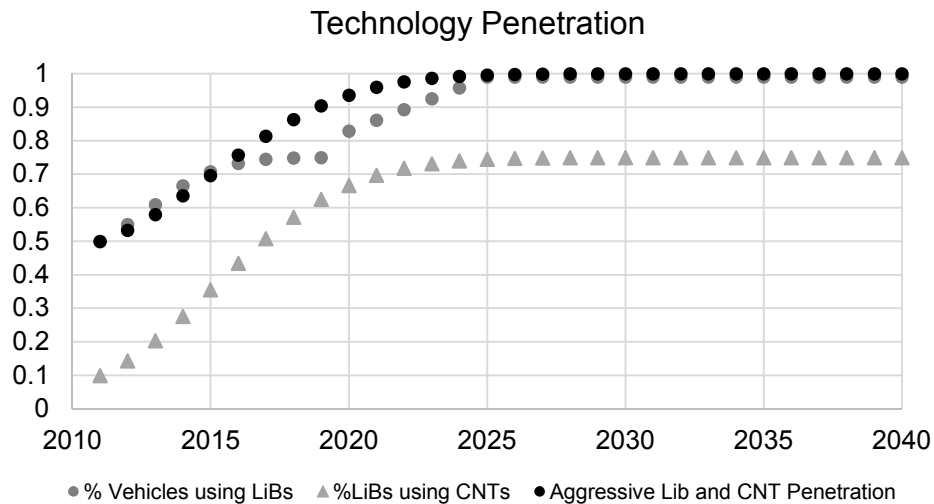


Figure 3.2 Penetration of a) CNTs used in LiB market and b) LiBs used in EVs over time

These estimates are very difficult to forecast given the scarcity of data and may vary depending upon the application. Because CNTs increase energy density, their use will be more beneficial in smaller-sized, portable applications. On the other hand, energy density and the high cost of large volumes of CNTs will be less beneficial and expensive for stationary applications, i.e. ESS. The same CNT penetration is used for each

technology, despite the fact that the penetration of CNTs will differ between the type of product in which the LiB will be used.

3.2.2 Life Cycle Impact Assessment

Life cycle assessment (LCA) assembles an inventory of the materials and energy necessary for producing, transporting, using and disposing of a good or service. LCA also requires an impact assessment step, wherein the “impact” on human or environmental health that result from all the necessary processes is calculated. The impact category is chosen by the LCA practitioner and determined by the overall goal of the study. No existing impact methodologies have incorporated capabilities to calculate the impact of nanomaterial emissions; while the previous chapter developed a method for assessing ecotoxicity for specific case study materials, this chapter will take a broader view of environmental impact than only ecotoxicity. Therefore, any impact calculated here will take into account the materials and energy necessary for producing carbon nanotubes but will not include the impacts of nanomaterials themselves. To quantify the environmental impact of nanomaterials, the life cycle inventory of carbon nanotube production from a previous study [69] is replicated using Ecoinvent 2.0 data and the environmental impact is quantified using the ReCiPe methodology.

The modeled production process of CNTs by Chemical Vapor Deposition follows [69] and is used to connect the production of CNTs for LiBs to the resultant environmental impact. Inventory data are from Ecoinvent 2.0 and impacts are calculated in SimaPro 8.0 using ReCiPe 1.10. The midpoint impact categories calculated in this study are climate change, measured in kg CO₂ equivalents, human toxicity (kg 1,4

Dichlorobenzene-equivalents) and particulate matter formation (kg PM₁₀), which is. ReCiPe also calculates ozone depletion, ecotoxicity, resource consumption, aquatic eutrophication and other measures of adverse environmental impact.

3.2.3 Policy Discussion

The current policy environment relies upon existing tools and mechanisms that are incapable of handling the unique challenges presented by nanomaterials given the differences in ecological risk assessment methods for nanomaterials and traditional materials. The policy assessment uses the MFA and LCIA findings to answer the questions a) are the forecasted production volumes cause for concern given their potential risk b) are existing regulations adequate for the various types of exposure to nanomaterials and c) are nanomaterial emissions the important piece that should be regulated.

3.3 Results and Discussion

3.3.1 Case Study Results

The following graphs in Figure 3.3 depict the sales and stock forecasts for the case material technologies based on the methods and assumptions for the baseline scenarios only.

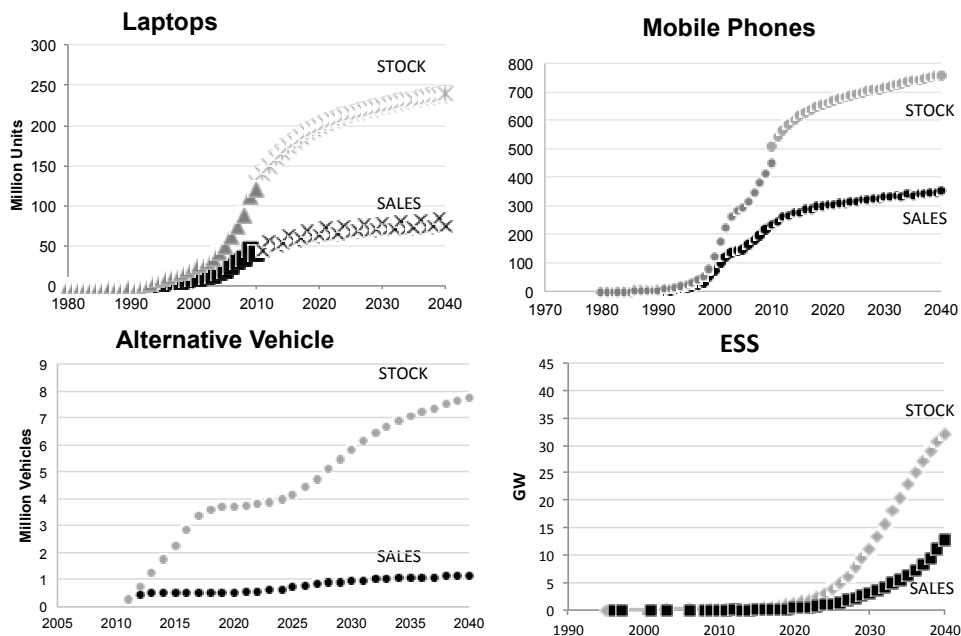


Figure 3.3 Baseline Forecasts for Nano-enabled Energy Products to 2040.

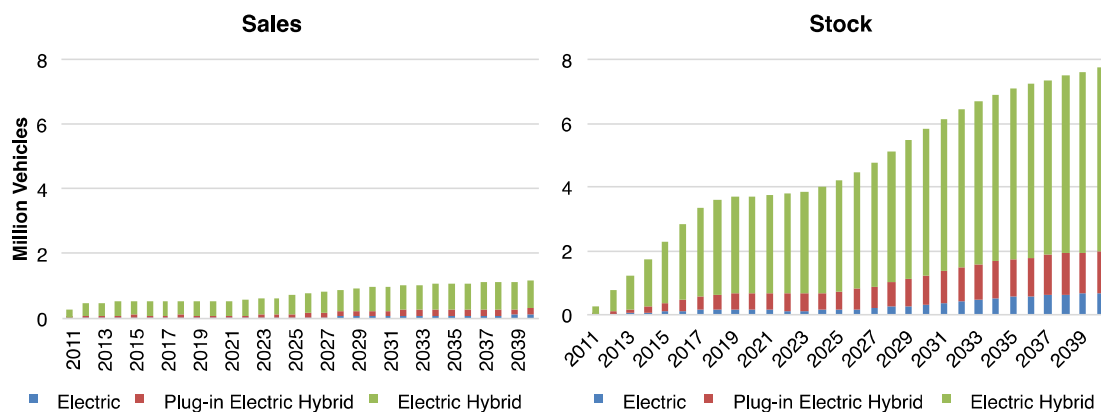


Figure 3.4 Breakdown of Alternative Vehicles Forecast by Electric Vehicle Types

3.3.1 Case Study Results

3.3.1.1 CNT Volumes

Based on the forecasts for the previous technologies (Figure 3.3) and the assumed intensity of carbon nanotubes per technology, the production, accumulated stock and volume entering end-of-life of CNTs is calculated in the context of the case study. The results show significant growth of CNT production over the future decades (Figure 3.5). Though the number of personal electronics is much greater and their lifespans much shorter, the larger mass of EV batteries leads to the result that CNT production for LiBs will correlate well with the demand for electric vehicles. However, in the future EES growth will be so significant that it will quickly dominate production by 2030 and 2035.

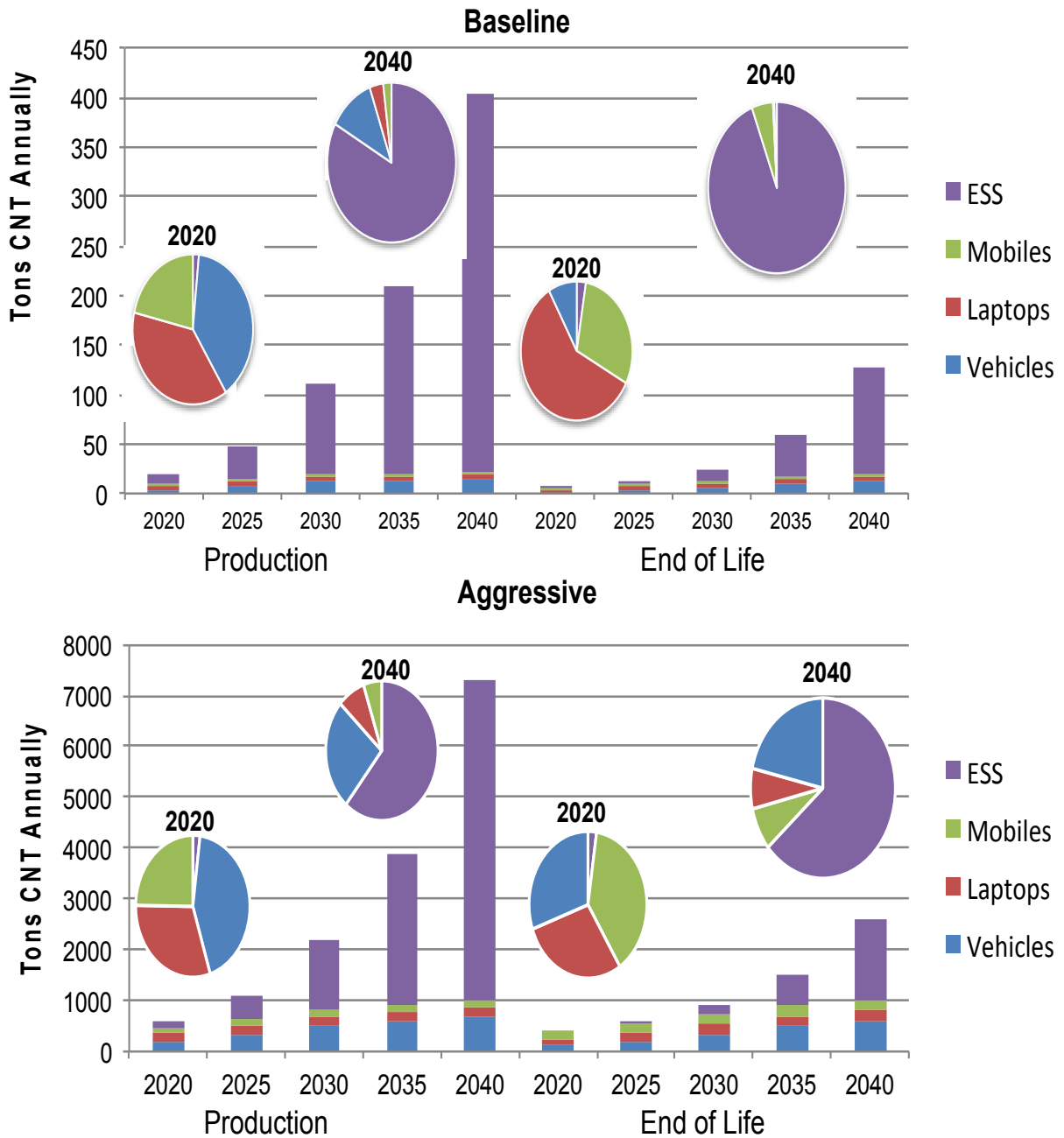


Figure 3.5 CNT production (left) and CNT entering end-of-life (right) through 2040 in the baseline scenario (top) and the aggressive scenario (below). *The pie charts depict the relative contribution of CNTs in 2020 and 2040 by technology type.*

The majority of CNTs entering end-of-life are from electric vehicle uses and ESS; however, it is notable that the overall mass of CNTs entering end-of-life is small, starting at less than 100 MT in 2020 and reaching just over 200 MT in 2040 for the entire US.

Due to the fact that ESS batteries have a longer lifespan than the rest of the products and that production of CNTs for EES is insignificant prior to 2030, CNTs from EoL ESS batteries never becomes significant in the timeframe analyzed here. However, given the production volumes forecasted in 2035 and 2040, the EoL volumes will rise dramatically after 2040.

The previous forecasts were based on baseline assumptions reasonable for each technology and its use given current knowledge. In order to determine the maximum volume of CNT production and emissions, the aggressive forecast incorporates 1) faster rates of technology growth 2) shorter lifespans 3) larger volumes of CNTs per battery and the percentage of batteries, which use CNTs. The aggressive scenario shows that production and EoL are approximately 20-50 times larger than in the baseline scenario. Given that the difference in CNT intensity is 10 times, this assumption is the most vital part of the forecast to influence the results.

3.3.1.2 Life Cycle Impact Assessment

Potential Impacts of CNT

The impacts are the result of raw material extraction, electricity production and emissions during the CNT production process. The environmental impact categories are assessed using ReCiPe and the midpoint impact categories are shown. These categories are displayed together in Figure 3.6 but should not be interpreted as comparable given the vastly different units in each category. The results show that the electricity needed for CNT production is the primary contributor, over 90%, of every impact category available in ReCiPe. Therefore, minimizing the environmental impact of CNT production for LiBs

or any application can be accomplished through electricity efficiency improvements or choosing a less energy intensive production process. The results use the baseline CNT production volumes and assume scale-up benefits in production, which reduces the per kilogram environmental impacts from up to 85% of those calculated in Chapter 2, as described in [121]. Chapter 2 uses the life cycle inventory from a bench scale production process, whereas scale-up in production will enable recycling of materials, and a reduction in energy usage when industrial volumes are produced. Specifically, the benefits assumed in this analysis are an electricity reduction of 87% of the lab scale process on a per kilogram basis, as well as complete recycling of the purification materials, primarily nitric acid. To demonstrate the benefit, the right-hand graph in Figure 3.6 shows the climate change impact using a lab-scale LCI and a scaled-up LCI (i.e. reduced electricity and recycled purification materials) on a logarithmic scale.

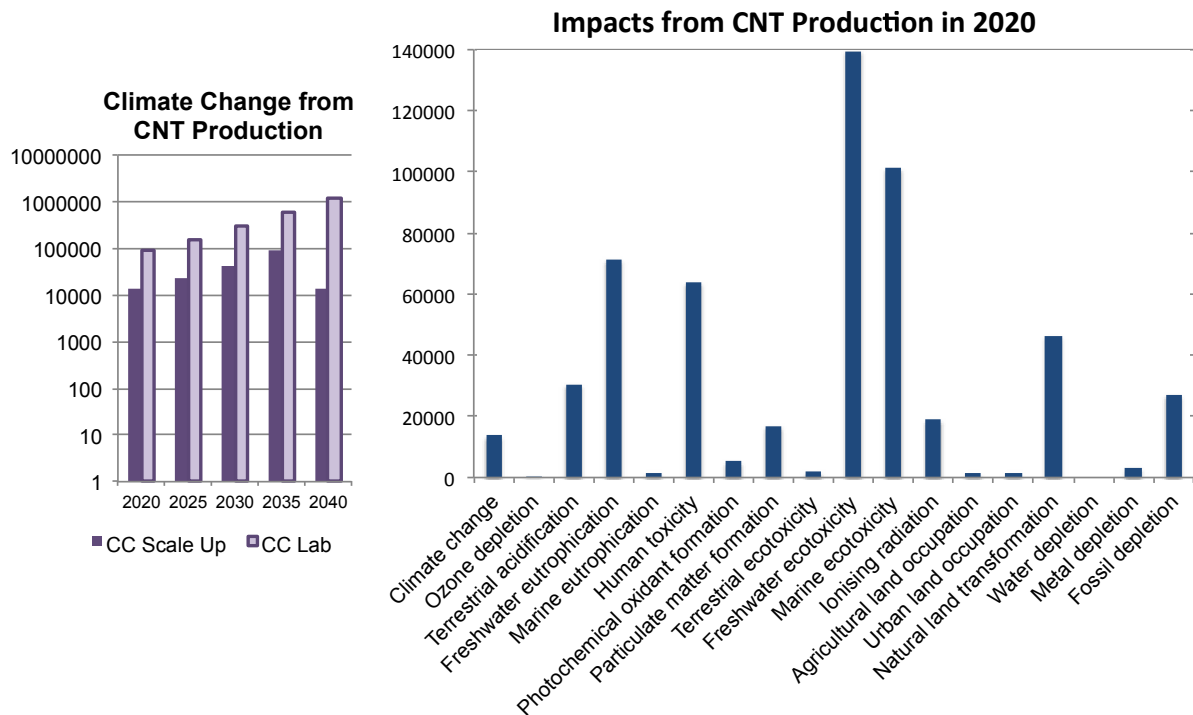


Figure 3.6 Impacts of CNT Production due to Embodied Materials and Energy:
right: Climate Change (y-axis: kg CO2 eq/yr) from 2020 to 2040.

Left: Impacts from CNT production in 2020 across all ReCiPe categories. The y-axis depicts kilograms in the impact categories listed in the table below.

Impact category	Units	Abbrev.
Climate change	kg CO2 eq/p/yr	CC
Ozone depletion	kg CFC-11 eq/p/yr	OD
terrestrial acidification	kg SO2 eq/p/yr	TA
freshwater eutrophication	kg P eq/p/yr	FE
marine eutrophication	kg N eq/p/yr	MEP
human toxicity	kg 1,4-DB eq/p/yr	HT
photochemical oxidant formation	kg NMVOC/p/yr	POF
particulate matter formation	kg PM10 eq/p/yr	PMF
terrestrial ecotoxicity	kg 1,4-DB eq/p/yr	TET
freshwater ecotoxicity	kg 1,4-DB eq/p/yr	FET
marine ecotoxicity	kg 1,4-DB eq/p/yr	MET
ionising radiation	kg U235 eq/p/yr	IR
agricultural land occupation	m2a/p/yr	ALO
urban land occupation	m2a/p/yr	ULO
natural land transformation	m2/p/yr	NLT
water depletion	m3/p/yr	WPD
metal depletion	kg Fe eq/yr	MRD
fossil depletion	kg oil eq/p/yr	FRD

The environmental impacts will grow over time directly with the production of CNTs since they are directly proportional to the mass of CNTs produced. Therefore, the demand for CNTs will directly drive the magnitude of impact, all things being equal.

The growth over time in each impact category, assessed by ReCiPe and pictured in Figure 3.6, depends on the growth in CNT production. This is because LCIA methods calculate “impact” by multiplying a characterization factor by the mass of the life cycle inventory. In the present analysis the life cycle inventory is not changed over time, and so the total impact depends entirely on mass of CNT production. The impact assessment results do not take into account emissions of CNTs during production or at any other point of the life cycle of CNTs because of the lack of data on their emissions and methods for impact assessment of nanomaterials; however, preliminary work shows that the upstream impacts of CNT production, i.e. raw material extraction and electricity production, outweigh the impacts associated with direct nanomaterial emission of CNTs [66].

These results reflect CNT use in LIBs alone, which is not a complete description of nanomaterial use in energy materials given that various other kinds of energy materials and nanomaterials belong in this category. The total impact, i.e. for all nanomaterials across all energy-related applications, will be considerably larger than those estimated here. The need remains to connect the increased production of nanomaterials and use through anticipatory governance mechanisms.

3.3.4 Metrics Discussion

The metrics that are used in LCA are often not directly useful to policy decisions despite the fact that many of the assessment tools used in LCIA and policy decisions are similar. This can be traced back to the fact that each research area uses its own set of metrics. Life Cycle Impact Assessment results often use “equivalency” metrics, such as climate change, measured in kg CO₂ equivalents, human toxicity (kg 1,4 Dichlorobenzene-equivalents), and particulate matter formation (kg PM₁₀-eq). The LCA Impact method ReCiPe also calculates ozone depletion, ecotoxicity, resource consumption, aquatic eutrophication, pictured in the results Figure 3.6. Risk assessment has its own set of metrics that include predicted environmental concentration (PEC), predicted no effect concentration (PNEC) for exposure assessment, toxicology metrics such as LOAEL, NOAEL, LC₅₀'s, which played an important role in Chapter 2, and finally, Risk Quotient (RQ) to compare exposure and toxicity. Policy decisions that aim to reduce these environmental risks often use specific mass metrics in the decision, for instance in the case of CWA or TSCA limit emissions of a specific contaminant in mass (kg) per time. Underlying the mass, monetary or mandate based metrics of policy is the

assumption that this will reduce an environmental impact. The following tables show the connections between risk assessment and LCA research, the metrics coming from those bodies of work, and the metrics used by policy to address the same or similar issues.

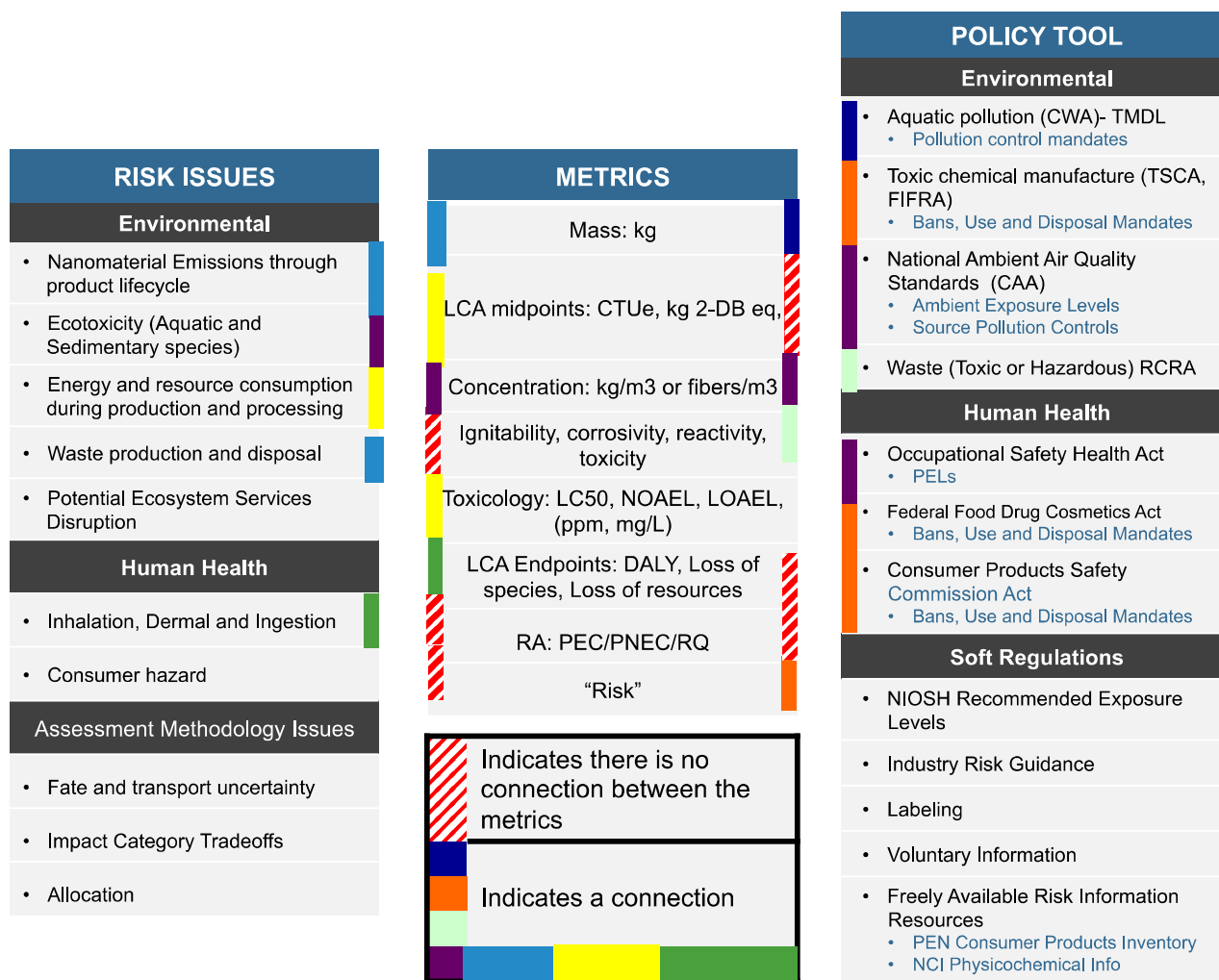


Figure 3.7 Endpoints and Metrics used in Risk Assessment Literature and Policy Mechanisms relevant to Nanomaterials. Colors correspond to similarities between metrics and risk assessment literature or policy mechanisms, respectively. Red diagonal lines there is no connection between risk literature and policy is not used.

The right hand side of Figure 3.7 outlines the regulations that have thus far been applied to nanomaterials and nano-enabled products. The regulations have analyzed nanomaterials as chemicals, water and air pollutants, waste, consumer hazards, and occupational hazards and end in mass metrics. This stands in contrast to the metrics

coming from risk assessment literature where effect assessment commonly measures a rate of adverse effect, exposure literature measures a predicted relevant environmental concentration, and life cycle impact assessment uses metrics for toxicity such as “cumulative toxic units” or kilogram equivalents to other toxic chemicals. While life cycle assessment offers a more holistic view of total environmental impact, it cannot describe what policies can result to reduce these specific impacts and the tradeoffs of implementing any policy. This makes it difficult to compare the results of our two results: the production of CNTs and the environmental impact associated with the embodied energy and materials.

Further confounding a comparison between embedded and upstream impacts in the present case study is the fact that the results from Chapter 2 can only compare freshwater aquatic ecotoxicity and not the full environmental impact. A life cycle framework can help contextualize both results and relate them to pertinent policies. To begin, the life cycle of the nanomaterials themselves is discussed to highlight important current policy discussions.

3.3.3 Case Study Policy Discussion

3.3.3.1 Regulating Nanomaterial Exposures:

As outlined in the scope in Figure 3.1 and Figure 3.8, federal policies will influence the production and emissions of nanomaterials throughout their life cycle. Those policies in the scope of the present case study on CNTs for LiBs encourage the development of new technologies utilizing nanomaterials, regulate occupational exposure policies that target exposure to workers, enforce waste policies that reduce exposure from manufacturing

waste, and enforce waste policies that target exposures that occur at the end-of-life of the nano-enabled product. The following is a look at these policies in order to understand the intersection of risk assessment and regulation at each step. The regulations discussed here attempt to reduce a broad range of environmental risks, i.e. all categories of environmental impact from Figure 3.6.

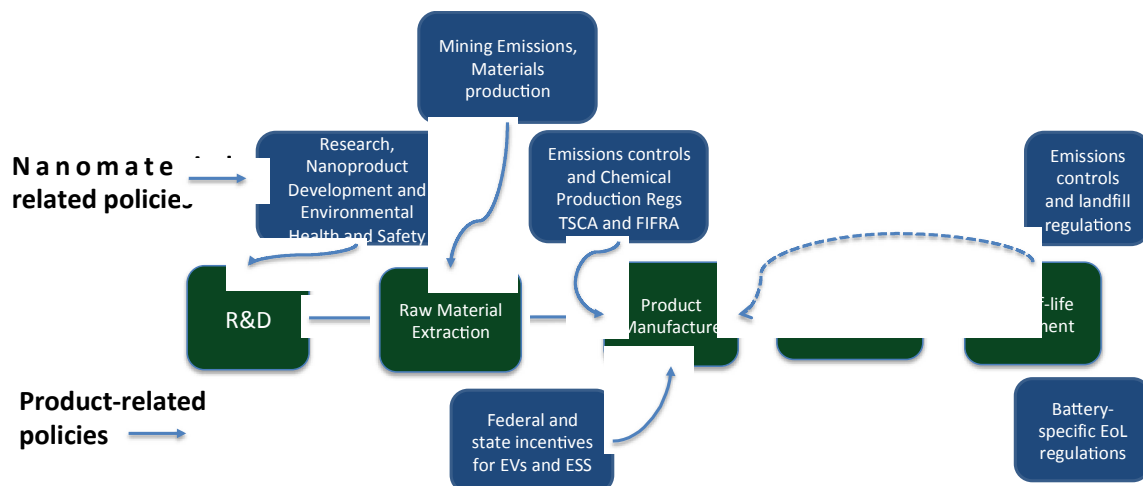


Figure 3.8 Life cycle Policies Related to the Nanomaterials, Nano Emissions and Nano-related Products.

Research & Development

There are multiple funding sources that encourage development of applications for nanomaterials. While it has been demonstrated that significant funding is coming from government and private entities for nanomaterial research and development, research for assessing the ecological risk of nanomaterials is relatively underfunded. The following table describes the amount of funding for Environmental Health and Safety projects under the National Nanotechnology Initiative in Fiscal Years 2006 and 2009. Research and development in EHS represents only 7% of the NNI budget for FY 2016, whereas Applications, Devices and Systems represents 26% [122].

	FY 2006		FY 2009	
Category	Number of Projects	Million \$ Invested	Number of Projects	Million \$ Invested
Instrumentation, Metrology, and Analytical Methods	78	26.5	42	11.3
Human Health	100	24	117	41.6
Environment	49	11.7	54	43.7
Human and Environmental Exposure Assessment	5	1.1	14	3.3
Risk Management Methods	14	3.3	21	3.5
TOTAL	246	66.6	248	103.4

Table 3.5 Federal Expenditures for Nanomaterial Environmental Health and Safety Research

While not directed toward promoting nanomaterials, the present study has shown that policies that impact the growth in grid energy storage and electric vehicles will in turn have a significant impact on nanomaterial demand. These policies include the CAFE standards that require automobile manufacturers to sell a given number of hybrid and electric vehicles. The dramatic increase in the sale of these vehicles will drive the production and ultimately the exposure of CNTs for batteries. Given the significant electricity requirements for CNT production, these requirements should take into account the embodied impacts of battery production.

Premanufacture

Before a chemical can be manufactured or used domestically, the prospective manufacturer must submit a pre-manufacture notice to the correct regulatory agency. The US EPA requires require pre-manufacture notification under the Toxic Substances Control Act (TSCA) and/or Federal Insecticide Fungicide Rodenticide Act (FIFRA) prior to production of chemicals, in the present case nanomaterials. These policies rely on Quantitative Structure-Activity Relationships (QSARs), Ecological Structure Activity

Relationships (ECOSARs) or chemical analogues to approximate chemical fate and toxicity. The resultant risk assessment is then the basis for the decision on whether to allow the manufacturer to begin production. Approximately 90% of PMNs are allowed without further regulation or information [123]. If there is insufficient information, the risk assessor can require the manufacturer to submit all risk information that they may have in order to assist in the risk assessment process. These assessments are difficult since the assessor requires a large amount of information in a short period of time. While these policies have a positive outcome, i.e. mandatory manufacturer risk information generation improves the quality of the risk assessment, one can imagine the difficulty in attempting to make a policy decision using inadequate models under a time constraint.

Other agencies such as Environment Canada, Department of Toxic Substances Control in California, and the European Union under REACH (Registration, Evaluation, Authorisation and Restriction of Chemical substances) have all held mandatory and voluntary risk reporting programs to generate the best available risk information. Under REACH, materials are either regulated if produced in large quantities or as hazardous substances if information on toxicity is well established. The requirement for pre-manufacture notice under FIFRA is binding given that the producer wants to manufacture over a threshold limit, measured by mass. The present case study predicts that domestic production of CNTs has already exceeded this threshold, and indeed risk assessors performing under TSCA have wrestled with CNTs and carbon-based nanomaterials. Whereas manufacturers have been allowed to produce these materials, the standards for nanomaterial emissions and pollution controls are strict in order to ensure no undue risk is introduced. The life cycle stage post-manufacture is also handled by these regulations.

The agreement between the EPA and the manufacturer settles the conditions under which nano-containing wastes are disposed.

Manufacture

During manufacture and up until the nanomaterials are transported to consumer use, occupational exposure policies will be relevant. Occupational exposure policies are critical for reducing the amount of exposure workers that handle these materials. This is an especially important case because, as compared to ambient environmental exposures, occupational exposures will be direct and at relatively high concentrations. One of the most prevalent examples of occupational exposure regulations are Occupational Safety and Health Administration's (OSHA) permissible exposure limits (PELS) and NIOSH Recommended exposure limits (RELs). NIOSH has set the REL for CNTs at $1 \mu\text{g}/\text{m}^3$ as an 8-hr TWA.

End of Life

End of life will be relevant in an interesting way for the present case study. While many nano-enabled products may be disposed of in a landfill this is not true for nanomaterial-containing batteries. Those nano-containing products that will be disposed of in a landfill or incinerated are likely those with little value when recovered and those that incur consumer exposure to nanomaterials. Given that the present study relates to batteries, it is significant to note the battery-specific disposal regulations.

Previous EPA analyses have estimated recycling rates for end of life electronics to be 18-22% [111], which in turn could result in some occupational exposure of CNT

without implementation of adequate protective measures. There is some evidence that CNT could be recovered during the recycling processes, but recovery and reuse of CNT is excluded from the present study since the mass of CNTs in each battery is small and recycling technologies are not yet equipped to recover this material. Given the small volume of CNTs entering EoL through 2040 and the modest recycling rates, occupational exposure will be a small hazard due to the relatively small volume of CNTs in EoL batteries. However, recycling of lead acid batteries for traditional *non*-electric vehicles are recycled at much higher rates, over 90%, indicating that EV batteries could benefit from the established vehicle battery regulations and collection infrastructure.

Various forms of landfill battery bans exist at the state level such as the rechargeable battery landfill bans in California and New York [124]. The hazard presented by landfill disposal of nanomaterial-containing products is poorly characterized since their fate and transport in such an environment is difficult to characterize. However, other disposal scenarios, such as shredding or incineration of batteries or electronics, will indeed present a hazard, because of a) high and direct inhalation and dermal exposure [125] to workers, b) current respirators will not be able to contain nanoparticulates [126], and c) inhalation is generally thought to pose a threat to human health (see Section 1.3). While occupational exposures may come into play given the recycling processes, the current case study does not predict an overwhelming waste stream in the near future and so the technology for detection of airborne nanoparticles may have evolved by the time that occupational controls will become more important.

3.3.3.2 Regulating the life cycle impacts of nanomaterial production

While the previous study finds that funding for R&D, TSCA PMN requirements, OSHA PELs, and battery disposal regulations will all intersect with the product of CNT for LiBs, the LCIA section found that there were other impacts relevant to nanomaterial production. Notably, CNT production has a high electricity requirement [69], [66]. Given the projected rapid increase in CNT production, the amount of electricity produced for CNT manufacture will likewise skyrocket and have its own implications for policy.

Electricity production is an already well-regulated industry. For instance, CAA regulations will control the particulate pollution coming from traditional electricity production methods. These regulations are increasingly tough for polluting electricity producers. The future forecast of environmental impact coming from CNT production would then be difficult without making assumptions about the future of electricity regulations. However, despite the fact that electricity regulations exist and are increasingly tough, there is a demonstrated impact from electricity production in the present analysis and as such there is room for improvement.

Future Policy Potential

Given that risk assessment knowledge is unable to keep up with the rapid pace of nanomaterial production, federally funded R&D efforts which should take into account these challenges and demand risk information be generated as a stipulation. If planners are to support the use of nanomaterials with federal funding for R&D and nanomaterial production start ups, then mandatory provisions about renewable and clean energy sources could lessen the resultant environmental burden. Last, end of Life Battery-

specific regulations should tie in the new risks of nanomaterial by using NIOSH RELs during shredding and developing guidelines for safely disposing of nano-containing wastes.

3.4 Conclusions and Future Work

The new challenges presented by nanomaterials include research and regulation metrics, based upon physicochemical characteristics other than mass, a broad variety of uses in consumer products and industrial applications, and fate/transport and transformations in the environment are not well understood or predictable. The case study of carbon nanotubes for the future of lithium ion batteries showed an increase in the demand for CNTs, which correlated well with the demand for electric vehicles through 2030 and thereafter was driven by new energy storage deployments. Using LCA tools to complete impact assessment showed that electricity was the main contributor to any environmental impact category. However, impact assessment tools are unable to include the impacts of nanomaterial directly, which remains a limitation in the impacts calculated here.

The ability of current regulations to reduce nanomaterial risks were mixed. Current regulatory tools (PELs) for reducing hazards of CNTs may not be stringent enough to protect workers, though control banding offers promise as a soft law mechanism for predicting the correct level of regulatory stringency with the least amount of information. The amount of PM₁₀ emitted for the predicted amount of CNT production will be insignificant when compared to current PM₁₀ emissions from all environmental and anthropogenic sources. Regulatory agencies that administer chemical

manufacturing and use policies struggle to produce decisions without the necessary risk information.

In addition to the environmental issues that policymakers must grapple with, a smooth transition into the public sphere will contribute to the success of NMs. These issues include public education, increased support for EHS research and programs, and increasing clarity and communication. Consumer education about the real costs and benefits of nanomaterials will be necessary to prevent adverse public opinion. Requiring detailed industry reporting about products containing nanomaterials could help understand where risks can be expected and where they already exist. Incentivizing safe development is key and can be accomplished by working with industry to gather risk information and increased support for Environmental Health and Safety research. Future policy can begin soft and become more inflexible/enforceable as risk knowledge becomes more certain and as nanomaterials increase in production volumes.

CHAPTER 4. Conclusions

The challenges in establishing risk reduction and adequate regulations for ENM are daunting, but many lessons have already been learned. While the exact methods necessary for reliable risk assessments are still under development, sustainability assessments can help understand the impacts of nanomaterial assessment in a broader context. This dissertation showed that scenario analysis gives context to the risks presented by nanomaterials by comparing the impacts of nanomaterials to other drivers of impact, especially upstream and direct electricity production. First, despite the multitude of physicochemical characteristics that influence the overall toxicity and behavior of ENM, ranges for the necessary factors were constructed and incorporated into life cycle assessments. Overall, despite the great uncertainty in modeling these characteristics, electricity is the primary driver of freshwater ecotoxicity in many of the scenarios. The exception to this trend was nanosilver, which requires more complex modeling and treatment of its dissolution into ionic silver.

The second example of ENM risk in context was the production of CNTs for LiBs. While the demand for LiBs is continuing to experience much growth, the drivers of demand can be narrowed to a few major technologies. These technologies, EVs and ESS, require large batteries in uses that are well regulated, vehicle batteries, or industry-held, i.e. energy storage systems are operated and owned by comparatively few stakeholders. The production of CNT will increase dramatically and is influenced most directly by the volume of CNTs used in each battery, even though CNTs make up a small percent of the active material.

Last, there are potential problems that could occur as the demand for nano-enabled products continues to grow. Life Cycle Assessment, while useful at defining the total impact of a product or service, is difficult to use in conjunction with policy decisions. In order for a future LCA-informed policies would have to take into account the tradeoffs between increasing CNT production and the overall energy footprint of this material. LCA allocates the environmental impact of electricity production used in nanomaterial manufacture to the *functional* unit, which in this case could be either the CNT, the LiB or the technology that uses the LiB. However, policy decisions using existing tools do not use the same kind of allocation techniques since policies analyze a smaller scope than LCA, i.e. the electricity producer and not the user of the electricity. Future policy should plan a future energy system that increases clean energy but not at the cost of shifting pollution from the traditional technology to electricity production for CNTs.

APPENDICES

Appendix A

Table A.1 NanoTiO2 Nanotoxicology Results

TiO2 TOXICITY RESULTS					
Environmental medium		LC50	LC 50 (Mg/L)	CHARACTERISTICS OF ENM	REFERENCE
Algae		72h growth inhibition	16	fine TiO2	[127]
			21	ultrafine TiO2	
		72 h growth rate based on nominal concentrations	61	fine TiO2	
			87	Ultrafine TiO2	
	Phaeodactylum tricornutum		10.91	Anatase 15 nm	[128]
			11.3	anatase 25 nm	
			14.3	anatase 32 nm	
			35.51	anatase 44 μm	
			24.11	rutile, 1 μm	
	Bacteria	B. subtilis		1000	
E. coli			2000		
Daphnia		48h tox	>100	--	[127]
			200	--	
		72 h tox	1.3	Anatase 15 nm	[128]
			3.15	anatase 25 nm	
			3.44	anatase 32 nm	
			250.3	anatase 44 μm	
			94.71	rutile, 1 μm	
			2.24	rutile, anatase mix	
Rotifer	Brachionus plicatilis		5.37	Anatase 15 nm	[128]
			10.43	anatase 25 nm	
			267.3	anatase 32 nm	
			107.4	anatase 44 μm	
			5.37	rutile, 1 μm	
Fish	Rainbow trout	96 h tox	>100	--	[127]
			200	--	

Table A.2 C60 Fullerene Toxicology data

ENVIRON- MENTAL MEDIUM	ENDPOINT	LC 50 (mg/L)	CHARACTERISTICS OF ENM	REF
Daphnia magna	48 hr toxicity	No LC ₅₀ calculated	C ₆₀ -malonate	[52]
			C ₆₀ -malonate gcd	
			C ₆₀ - gcd	
			thf-nc60	
			aqu-nc60	
	48 h tox	0.8	Thf-nc60	[130]
	48 h tox	>35	Aq-nc60	
	Immobilization	9.344	aq-nc60	[130]
	48h tox	10.515		
	delay molting	2.5		[131]
	reduce offspring	5		
	48 h tox	0.46	Thf-nc60	[132]
		7.9	Sonicated c60	
	48 h lc50	0.44	THF-nC60, mature mother daphnids	[133]
	48 h lc50	0.2	THF-nC60. neonate (gestating) daphnids	[133]
	altered molting, and decreased reproductive output observed		Aqu-nc60	[131]
Daphnia, hyalella, Marine copepods		>22.5	Aqu-nc60	
E. Coli	E. Coli toxicity	no LC ₅₀ calculated	Thf-c60	[134]
			aqu-nc60	
			c60oh24	
			pvp-c60	
T. platyurus	24 hr tox	>463		[135]
Fathead minnow	48 hr tox	100% mortality at .5 ppm		[50]
Fish	biomarkers of lipophilic xenobiotic exposure,	not adequate to assess nC60 exposure effects at concentrations up to 0.5 ppm for 96 h	water stirred nc60	[131]
L. variegatus	no lc50 calculated	Survival, growth, reproduction, and feeding rates	c60, water stirred	[136]
Lumbricus rubellus	no lc 50 calculated	mortality, growth and reproduction	Water stiired nc60	[137]

Table A.3 Nanosilver toxicology results

NANOSILVER TOXICITY RESULTS			
Environmental Medium	Type of NM	LC50 (mg/L unless marked)	Reference
Daphnia, ceriodaphnia	Ag-Cit	1.5 µg/L	[138]
	Ag-PVP	2 µg/L	
		0.04	[139]
		0.067	
		0.1	
		56.73 µg/L	[51]
		153 µg/L	
	Ag-Cit	0.15 µg/L	[140]
	Ag-Cit+ 4 mg/L SRHA	0.7 µg/L	
	Ag-PVP	2 µg/L	
	Ag-PVP+4 mg/L SRHA	5.7 µg/L	
	Ag-Cit	0.004 µg/L	[141]
		0.002 µg/L	
		0.187 µg/L	
Crustaceans: Thamnocephalus platyurus		207.75 µg/L	[51]
		279.2 µg/L	
Fish: Minnow, zebrafish (danio rerio)		9.4	[142]
		1.25	
		10.6	
		1.36	
		7	[138]
Algal P subcapitate	Ag-Cit	3 µg/L	[140]
	Ag-Cit+ 4 mg/L SRHA	5.2 µg/L	
	Ag-Cit+ 8 mg/L SRHA	5.6 µg/L	
	Ag-PVP	19.5 µg/L	
	Ag-PVP+4 mg/L SRHA	36.7 µg/L	
	Ag-PVP+8 mg/L SRHA	48.9 µg/L	
	Ag-Mic	966 µg/L	
Algal P tricornutum	Ag-Cit	2380 µg/L	
	Ag-PVP	3690 µg/L	

Table A.4 SWNT toxicology results

SWNT TOXICITY RESULTS			
Medium	Endpoint	LC50 (mg/L)	Ref
Daphnia	reproduction reduction, 21 days	50	[52]
	reproduction reduction, 21 days	50	
	acute toxicity- 48 hr	6060	
	acute toxicity- 96 hr	50	[143]
	immobilization	1.306	[144]
	mortality	2.425	
Fish	Respiratory toxicant	0.1	[145]
	Hatching delay	120	[146]

Appendix B.

Table B.1 Coatings and Functionalizations of Case Study Materials in Toxicology

Coating	nm	Primary particle size	Study type	Reference
uncoated	Ag		Tox: fathead minnow	[142]
		3.1	Tox: daphnids and	[138], [147]
		35 , and 600-1600 (micro)	Tox, uptake, daphnids, and fish hepatocyte cells (human cells too)	[139]
		18(HDD)	Bacterial growth	[148]
		20-30	Tox: ceriodaphnia, metplate	[149]
	C ₆₀	35.8		
			Differential toxicity to drosophila	[150]
				[151]
		517+-21 nm (HDD)	Agglomeration of C60 during ingestion and excretion	[152]
	C ₇₀			[151]
		656+-39 nm (HDD)	Agglomeration of C70 during ingestion and excretion	[152]
	SWNT		Differential toxicity to drosophila	[150]
			Immobilization and mortality	[52]
				[153]
	MWNT			[52]
		10-30nm		[154]
			Differential toxicity to drosophila	[150]

CIT (citrate)	Ag-Cit	14 nm	aquatic tox	[140]
		7+-11	Tox: nematode	[155]
		9.1+-4.2	Tox: E. Coli	[156]
		19.1+-6.0		
		43.5+-12		
		55.9	Tox: Daphnia magna and predator-prey interactions between dragonfly nymphs	[157]
		56.1 ± 13.8	Crop growth	[158]
		10 (HDD)	Bacterial growth	[148]
		11.6+-3.2	Stability in ecotoxicology media	[159]
		17+-5nm	Toxicity of Aqueous and Dietary Exp to Snails	[160]
PVP	Ag-PVP		aquatic tox	[140]
		8+-2	Tox: nematode	[155]
		38+-8		
		75+-21		
		17.9+-7.0	Tox: E. Coli	[156]
		79.7+-4		[161]
		6	Tox: crustaceans	[51]
		8		
		12 (HDD)	Bacterial growth	[148]
		10.8+-3.3	Stability in ecotoxicology media	[159]
	SWNT-PVP		Stabilization and Debundling method	[162]
	C60-PVP	4.4 (HDD)	Bacterial growth	[134]
Gum Arabic	Ag-GA	5+-2	Tox: nematode	[155]
		22+-6		

OH	MWNT-OH	20-30		[154]
	C60(OH) ₂₄	122 (HDD)	Bacterial growth	[134]
			Daphnia magna	[52]
			Toxicity: embryonic zebrafish	[151]
		153+-18	Histopathology of FHM	[163]
			Neutrophil function of FHM	
COOH	SWNT-COOH		Daphnia magna	[52]
	MWNT-COOH	20-30		[154]
CONH ₂	SWNT-COHN ₂		Daphnia magna	[52]
LPC	LPC-SWNT	1.2	Tox	[143]
			Tox	[144]
BPEI (branched polyethylenimine)	Ag-BPEI	23.3+-15		[156]
		10	Bacterial growth	[148]
PEG	SWNT-PEG			[52]
				[153]
	Ag-PEG	10.3+-3.2	Stability in ecotoxicology media	[159]

Appendix C.

Table C.1 ENM Substance Data

Input parameter , Abbreviation, Unit	Necessary? [81]	NanoTiO ₂		SWNTs		C60 Fullerenes		Nanosilver and Silver, respectively			
		Value	Ref	Value	Ref	Value	Ref	Value	Ref	Value	Ref
Molecular weight; MW g.mol ⁻¹	Yes	79.9	[164]	1e5	[165]	720.6	[166]	107	Based on silver	107	[167]
Henry law coefficient KH ₂₅ C Pa.m ³ .mol ⁻¹	No (set at 1E-20)	1E-20	--	1 e -20	--	1e-20	--	1e-20	--	1e-20	--
Partitioning coefficient between dissolved organic carbon and water KDOC L.kg ⁻¹	Yes	N/A	[83]	1e-20, 1e3	[165]	1e-20, 1e3	[165]	0.2-2.9	[168]	Logkd= 2.5,	[167]
Partitioning coefficient between suspended solids and water KpSS l/kg	Yes		--	1e-20, 1e3		1e-20, 1e3		0.2-2.9		Logkd=5.2	
Partitioning coefficient between sediment particles and water KpSd l/kg	Yes		--	1e-20, 1e3		1e-20, 1e3		0.2-2.9		=3.6	
Partitioning coefficient between soil particles and water KpSl l/kg	Yes		--	1e-20, 1e3		1e-20, 1e3		0.2-2.9		Log kd= 2.6,	
Degradation rate in water, sediment, soil, air kdegW, kdegSd , kdegSl , kdegA s ⁻¹	No (set at 1E-20)	1E-20	--	1e-20	--	1e-20	--	1e-20	--	1e-20	

Bioaccumulation factor in fish/biota BAF _{fish} l/kg	Yes	5.66×10^4 and 1.18×10^5	[169]	5e3, 5e-2	[170]	Log BCF= 2.984.40 - 3.674.16,	[171] [133]	.05	Based on silver	.05	
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Appendix D. Ecotoxicity Results

Figure D.1 Ecotoxicity of nanosilver by percent and actual value in all three scenarios

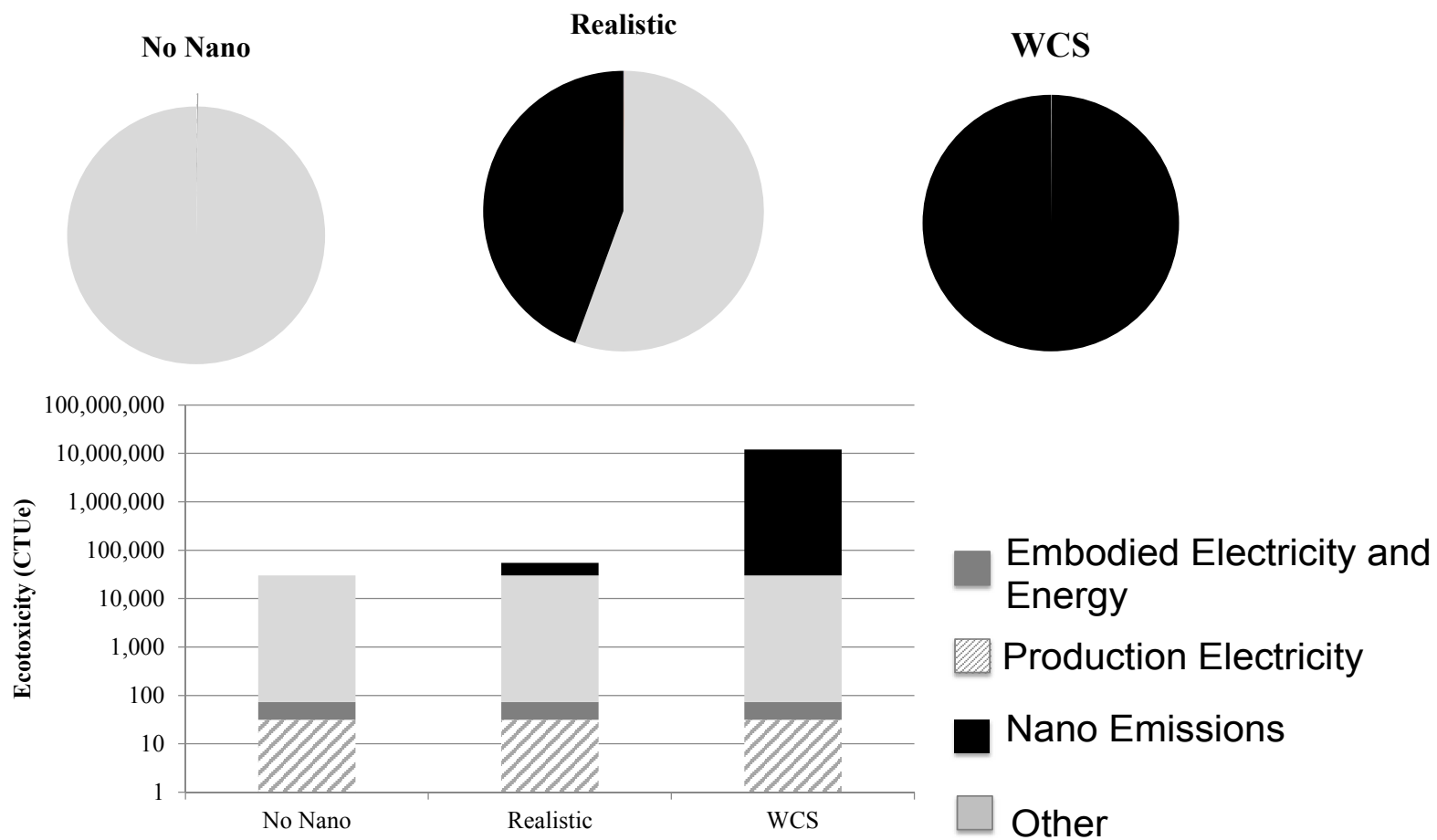


Figure D.2 Nanosilver impacts as broken down before categorization and presented on a log scale. *Silver mining is the primary source of ecotoxicity in both the no nano release and the realistic scenarios. In the worst case scenario, the nanomaterial release dominates ecotoxicity.*

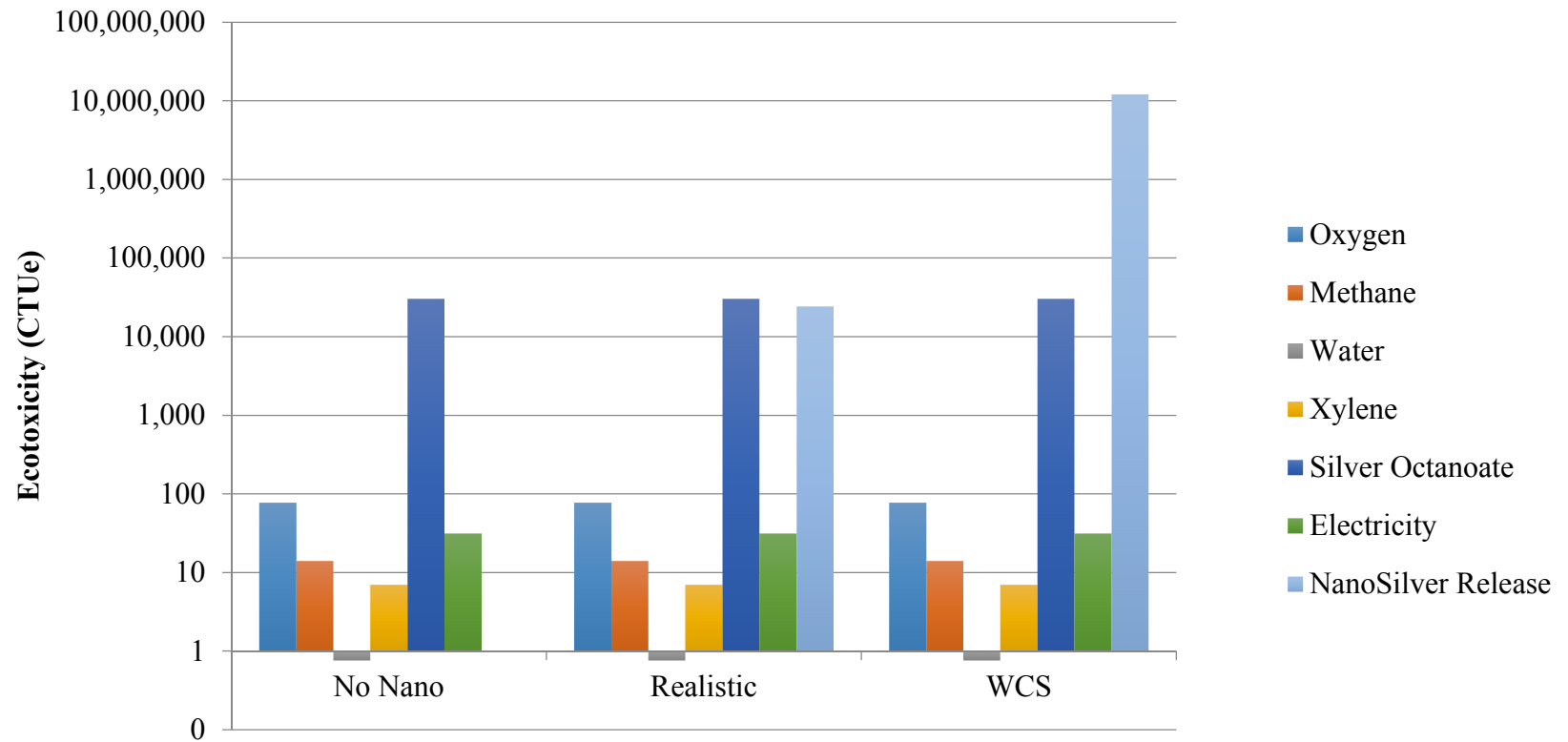


Figure D.3 Ecotoxicity of SWNT Production by the Arc Plasma Method

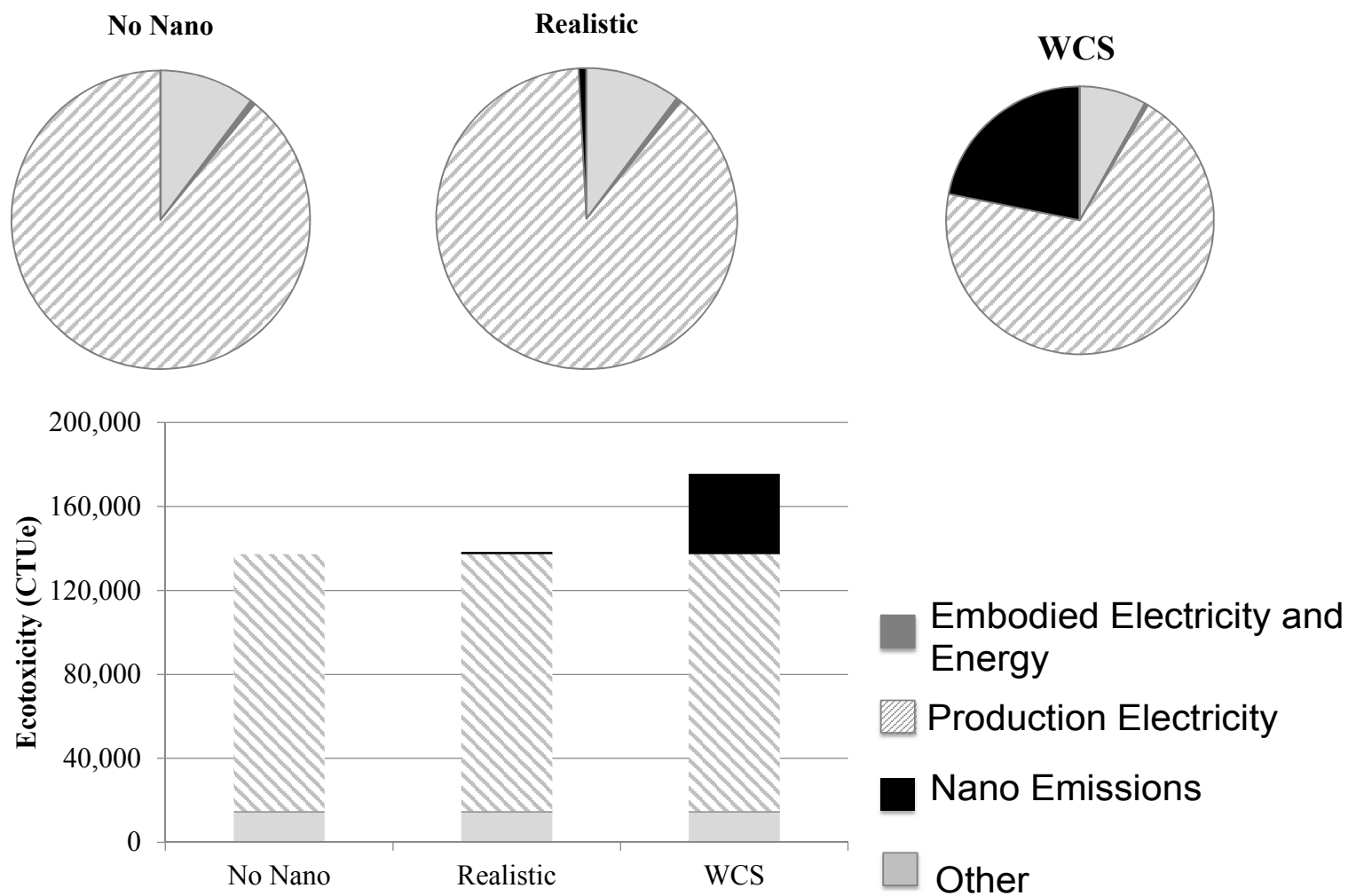


Figure D.4 Ecotoxicity of SWNT production by the CVD method

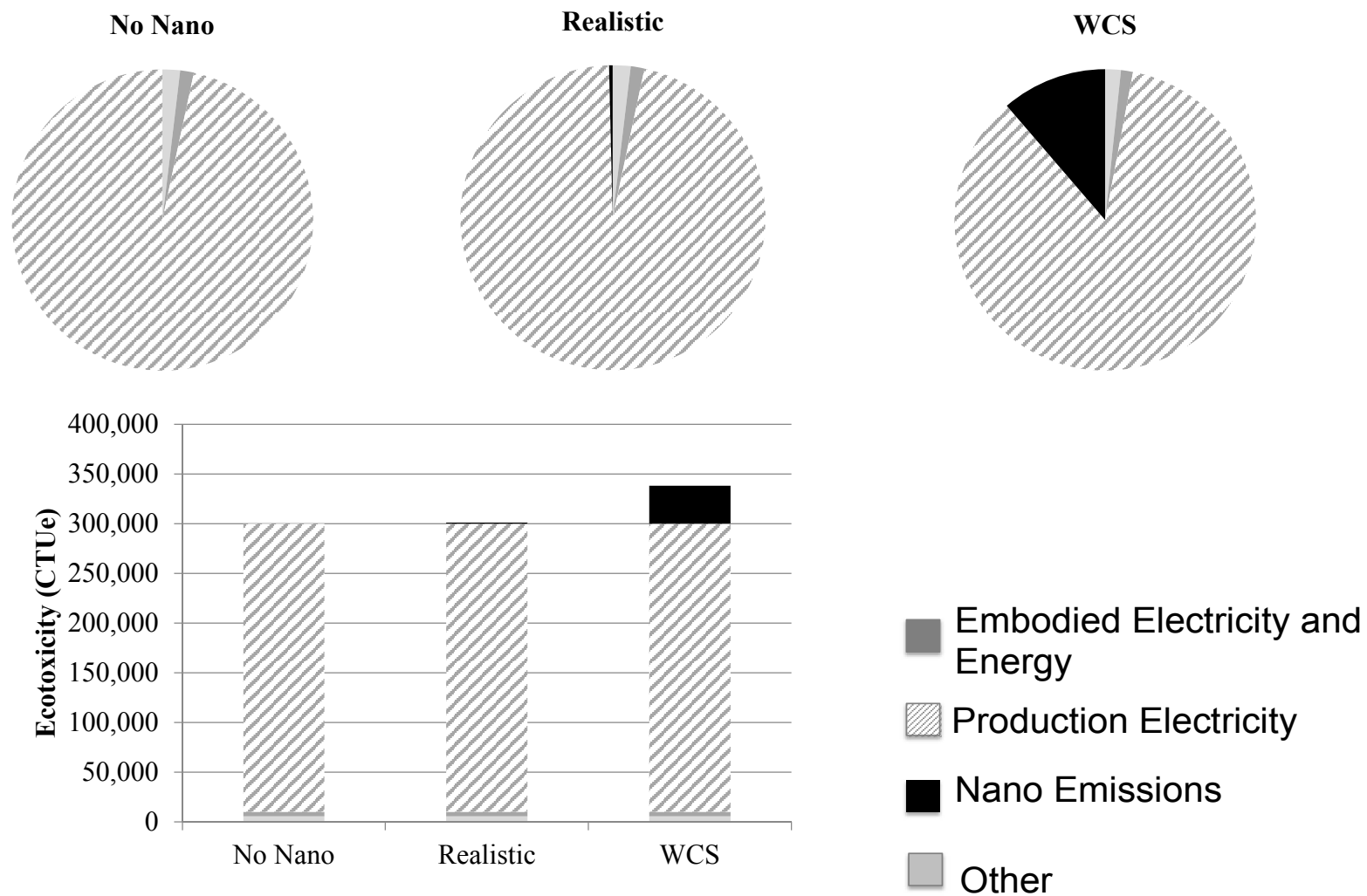


Figure D.5 Ecotoxicity of C60 Fullerenes production by the arc plasma method

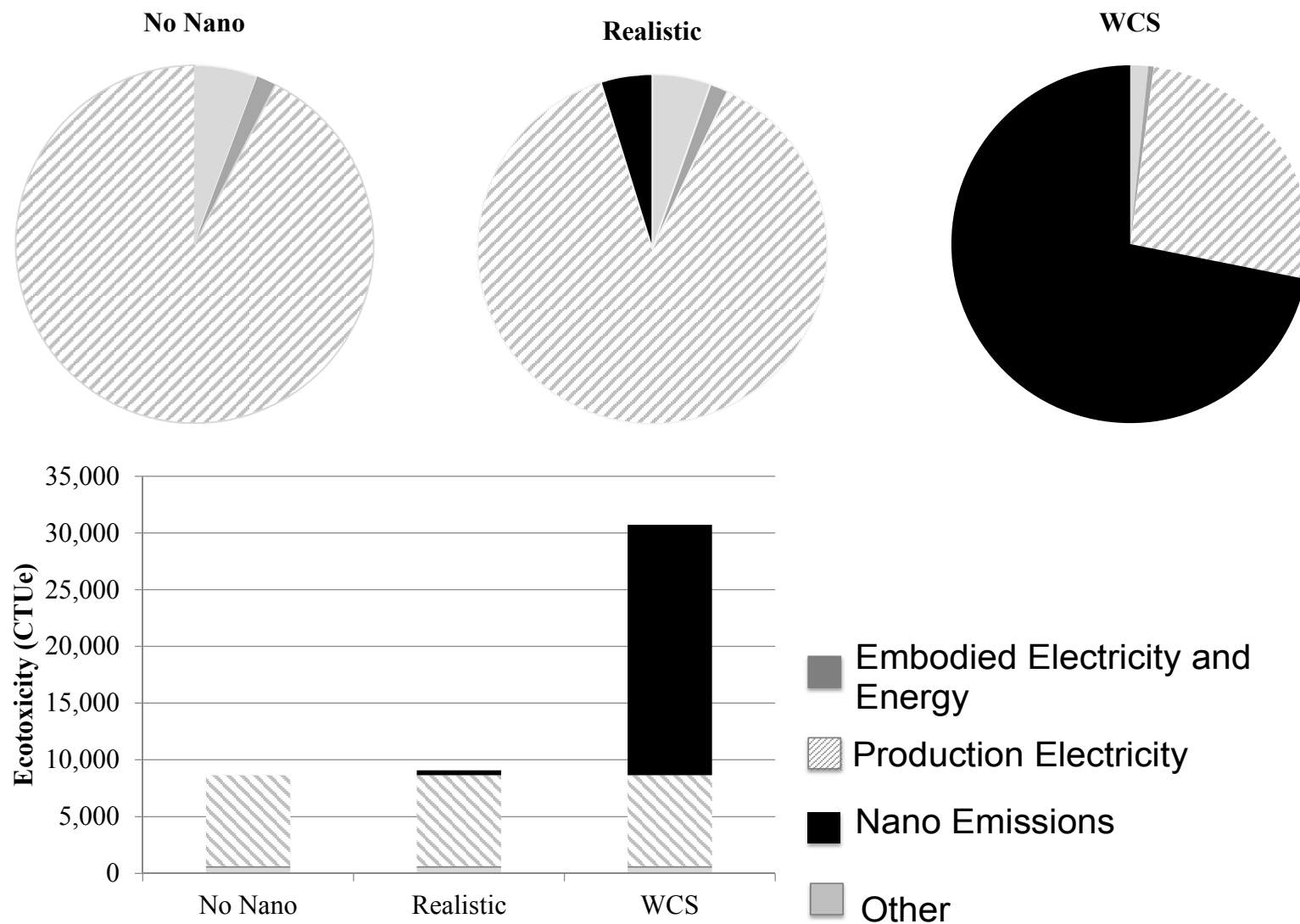


Figure D.6 Ecotoxicity of C60 Fullerenes production by pyrolysis.

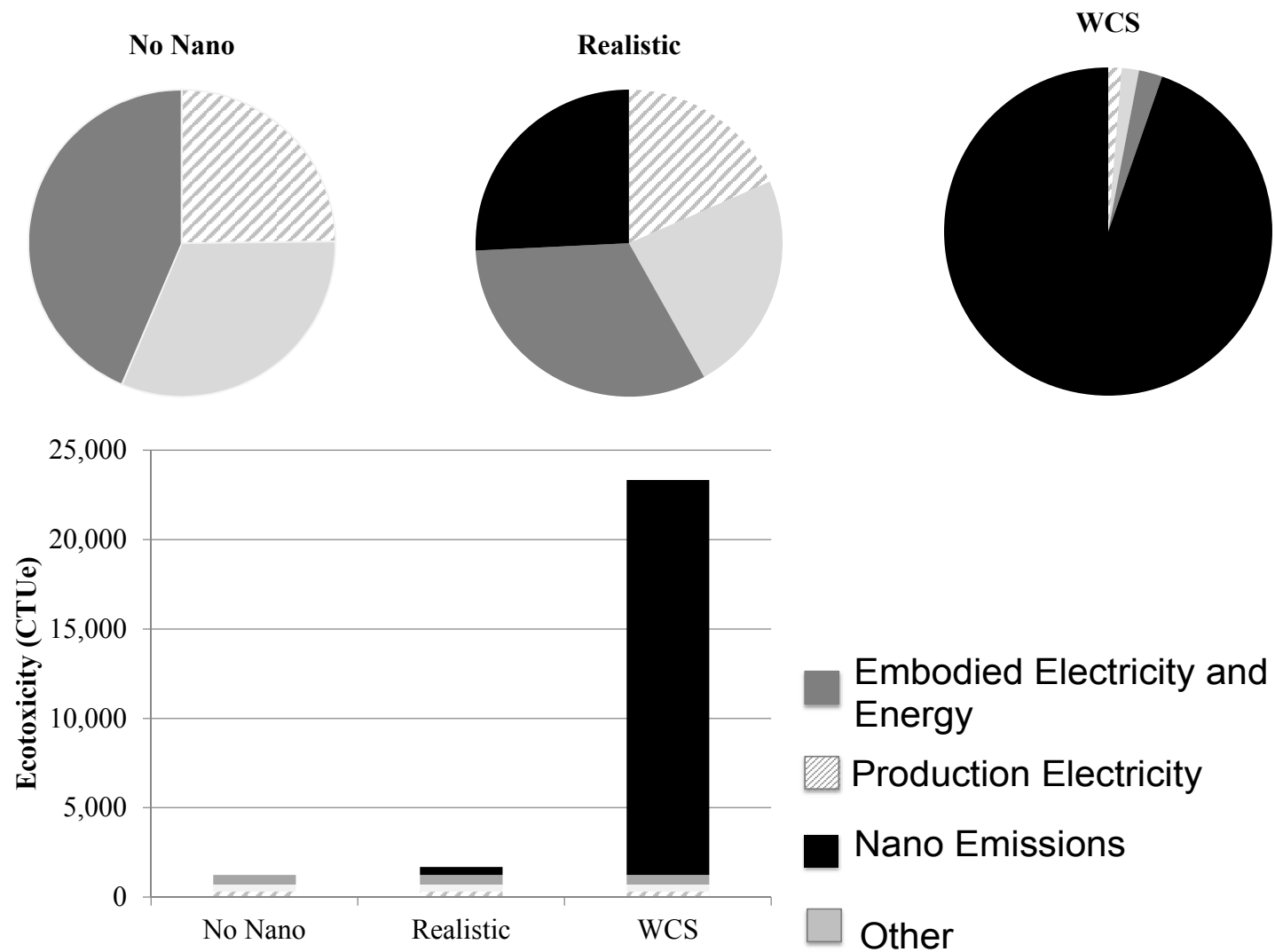
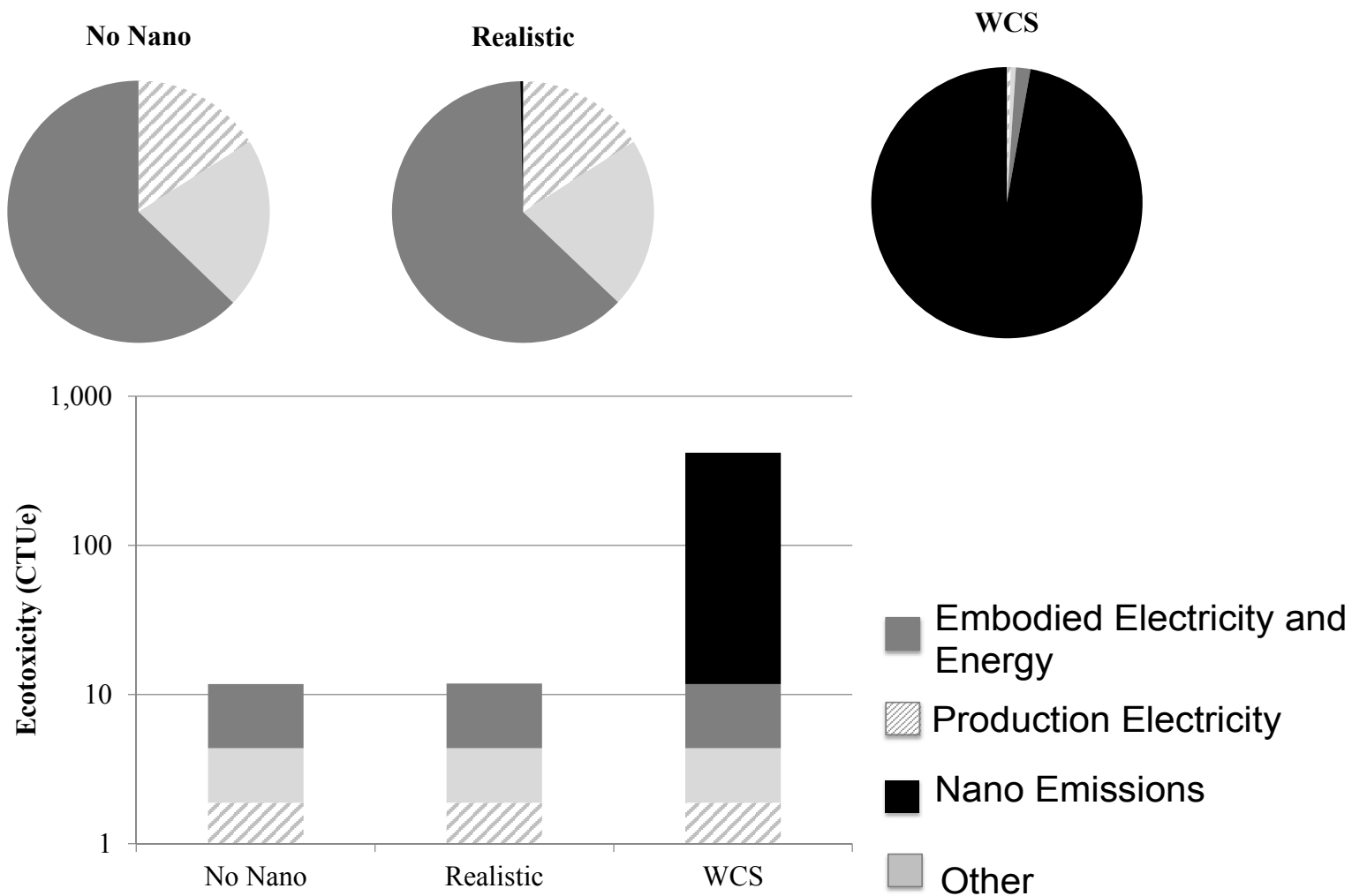


Figure D.7 Ecotoxicity of Nano-TiO₂ production.



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